Ion Exchange Nutrient Recovery from Municipal Wastewater

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ION EXCHANGE NUTRIENT RECOVERY FROM MUNICIPAL WASTEWATER

by

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ABSTRACT
ION EXCHANGE NUTRIENT RECOVERY FROM MUNICIPAL WASTEWATER

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Marquette University, 2013

Nitrogen and phosphorus discharge is regulated due to eutrophication. Typically ammonium-nitrogen is removed through nitrification which requires energy and phosphorus (P) is removed by metal salt addition to precipitate P. A more sustainable approach may be to implement nutrient recovery to form fertilizers. Most nitrogen fertilizer is formed through the energy intensive Haber-Bosch process. Phosphate rock, a limited resource, is mined for P fertilizer. Discharge regulations and the fertilizer production costs provide an economic driver for recovery. The current project used anionic and cationic ion exchange (IX) to concentrate the nutrients with recovery by struvite precipitation. Previous work lacks direct comparison of anion media, treatment of real wastewater with 2 IX columns in series, evaluation of regeneration characteristics and struvite precipitation from combined regenerants. During batch testing, Dow-Cu removed 76% of P while Dow-FeCu and LayneRT™ showed removal of >60%. These three media were tested in column mode using filtered municipal wastewater secondary effluent dosed with nutrients. Phosphate removal before breakthrough (PO_4-P effluent>0.075 mg/l) for LayneRT™, Dow-FeCu, and Dow-Cu was 2.00, 1.49, and 0.46 g P/L_{BV}, respectively. Desorption of >89% occurred for all 3 resins. Dow-FeCu provided the best conditions: effective removal, efficient regeneration at neutral pH and high (560 mg/l) regenerant P concentration. Natural zeolite was used for cation exchange. During ammonium exchange batch tests, NaCl solution with pH<13 was optimal for regeneration of zeolite. Column testing of zeolite was conducted using effluent from the LayneRT™ column. Capacity during IX cycle 1 and 2 before breakthrough (NH_4-N effluent > 1.5 mg/l) was 3.9 and 6.1 g N/L_{BV}, respectively; performance variability is due to the difference in influent cation concentrations. Desorption was 74% and 68% in cycle 1 and 2, respectively. Struvite was precipitated from zeolite and anion regenerant with 71%, 13%, and 74% P removal for LayneRT™, Dow-Cu, and Dow-FeCu regenerants, respectively. Struvite precipitation was limited by Mg. Precipitates contained impurities such as Al^{3+}, Ca^{2+}, and Fe^{2+}. The IX-recovery process removed greater than 98% P and 95% N and formed solids containing 13% P and 2% N.

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DEDICATION

I would like to dedicate this thesis to my wife, parents, extended family and friends whose support throughout my life has allowed me to reach the point I am at today.

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1 Introduction and Literature Review

1.1 Redesigning Wastewater Treatment

The focus of this study was to more efficiently utilize resources in municipal wastewater for economic benefit while producing high quality effluent. In its traditional form, municipal wastewater treatment requires large energy inputs for biochemical oxygen demand (BOD) and nitrogen (N) removal and chemical inputs for phosphorus (P) removal (Jetten *et al.*, 1997; Metcalf and Eddy, 2003). The first project objective was to replace secondary aerobic treatment of organics with anaerobic treatment. Aerobic treatment requires large quantities of electricity, greater than 50% of all plant energy usage, to transfer air into the reactor, while anaerobic treatment could potentially produce a net gain in energy (McCarty *et al.*, 2011). Net energy gain would be accomplished through electrical generation from the anaerobic reactor's biogas. In addition, anaerobic treatment produces less biomass than aerobic treatment and therefore biosolids handling is reduced; biosolids handling is a costly component of wastewater treatment plants (Smith *et al.*, 2012). Despite these benefits, anaerobic treatment lacks nutrient, N and P, removal capabilities that are conventionally accomplished through nitrification/denitrification and enhanced biological phosphorus removal (EBPR) in aerobic and anoxic systems (Smith *et al.*, 2012). In addition to EBPR, phosphorus is also removed through chemical precipitation which uses metals to precipitate phosphate (PO_4-P). An alternative redesigned wastewater treatment process may take advantage of anaerobic treatment for energy recovery coupled with physical/chemical treatments targeting N and P removal and recovery.

N and P often must be removed from wastewater to meet regulatory discharge limits, but they are also valuable resources. In states with numeric criteria, total P and total N waterway limits range from 0.006-3.75 mg/l and 0.14-90 mg/l, respectively (USEPA, 2013). N and P are regulated due to eutrophication in the environment, which is excess growth of algae due to nutrient availability followed by their death, consumption by microbes and subsequent oxygen depletion; N is also regulated due to aquatic toxicity (Camargo and Alonso, 2006; Diaz and Rosenberg, 2008). These two macronutrients are potential resources as high crop yields are dependent on fertilizers containing N and P. In order to obtain N fertilizers, about 1% of the world's energy is used in the Haber-Bosch process that forms ammonium (NH_4^+) from nitrogen gas (N_2) (Smith, 2002). In wastewater treatment, additional energy is spent to convert the NH_4^+ in the wastewater back to N_2 through nitrification/denitrification; the N cycle as it pertains to fertilization and wastewater is depicted in Figure 1 (USEPA, 2010). A potentially more economical solution is to remove and recover NH_4^+ from the wastewater for use as a fertilizer.

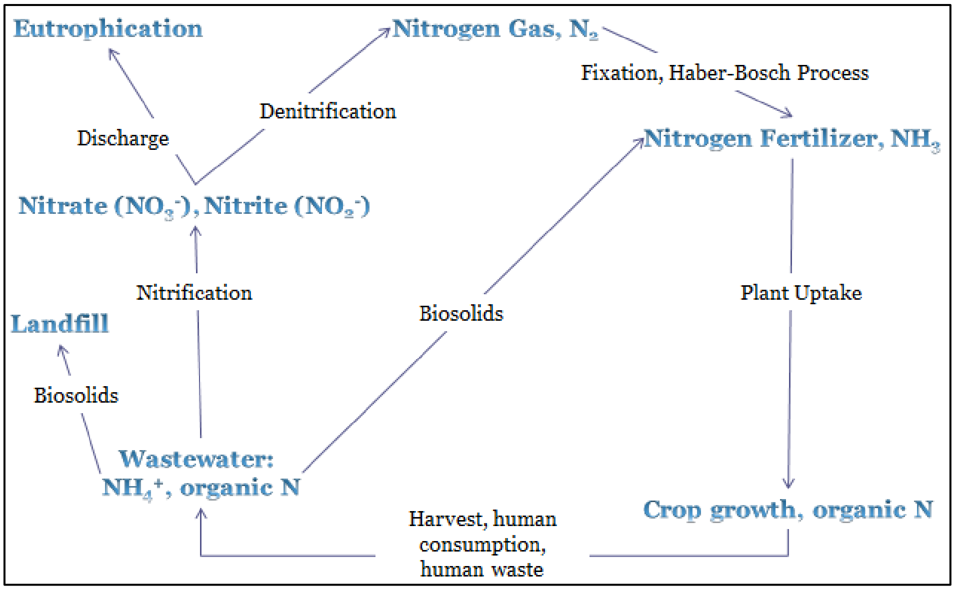

Figure 1: Simplified schematic of nitrogen cycle relating to fertilization and wastewater

Phosphorus fertilizer is currently obtained from mining, which introduces two main concerns: processing requires energy and phosphate rock supplies are expected to be depleted in 50-100 years (Cordell *et al.*, 2009). Therefore, recovery of PO_4-P from wastewater may be more sustainable than mining and traditional wastewater P removal by providing economic, environmental, and food supply benefits. Accordingly, the redesign of wastewater treatment considering improved sustainability must address nutrient recovery.

The anaerobic membrane bioreactor (AnMBR) has been proposed as the anaerobic treatment process and has the potential to reduce chemical oxygen demand (COD) and total suspended solids (TSS) to less than 80 and 1 mg/l, respectively (Gimenez *et al.*, 2011; Kim *et al.*, 2011). The treatment train can include a primary clarifier in series with an AnMBR. Solids from each of these processes are removed and can be sent to conventional municipal anaerobic digestion which is followed by solids dewatering. N removal could be implemented in the supernatant from solids dewatering, primary clarifier effluent, or AnMBR permeate; N removal technologies must be separate from the other treatment unites. P removal could be implemented anywhere in the system depending upon process selection. Specifically, precipitation of P could be performed in the clarifier, AnMBR, solids dewatering supernatant (SDS) or the final effluent. However, other P removal processes would only be applicable to the SDS or final effluent. A diagram one possible process is depicted in Figure 2.

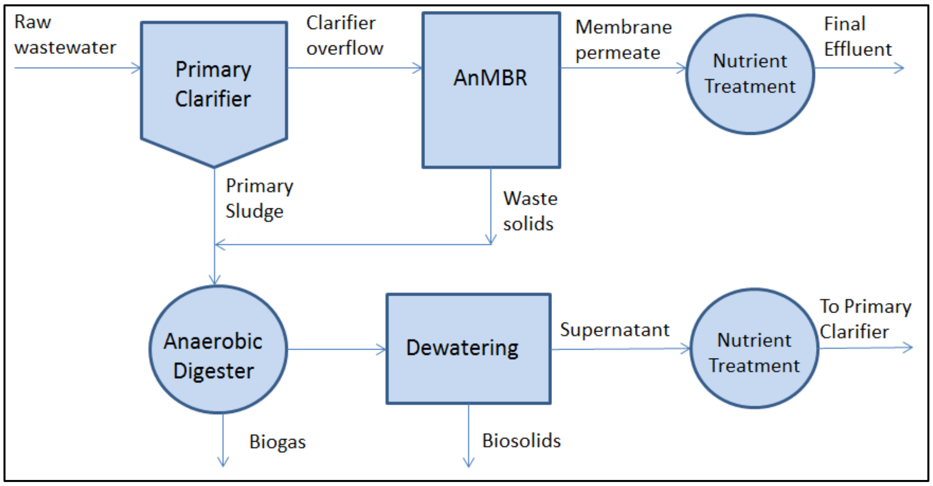

Figure 2: Process diagram for anaerobically treated municipal wastewater

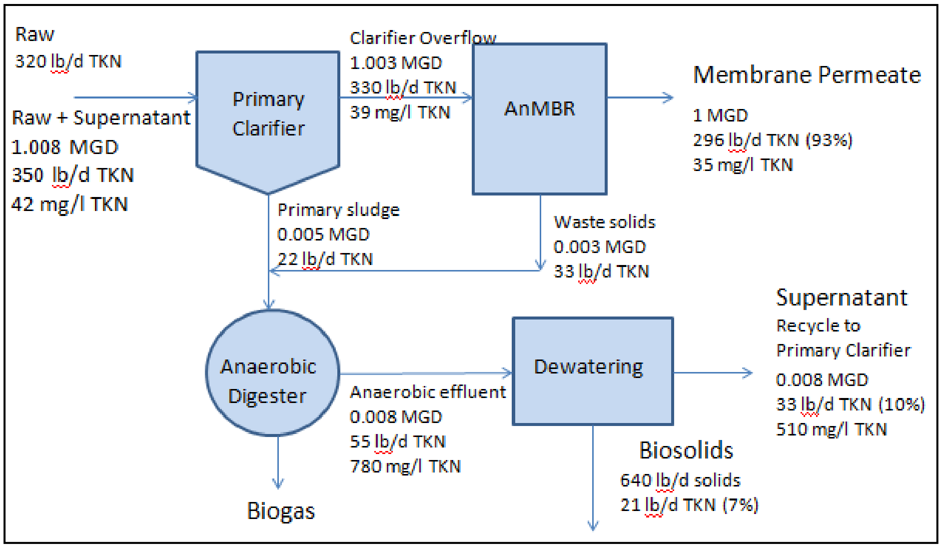

Figure 3: Estimated N balance for 1 million gallons per day (MGD) anaerobically treated municipal wastewater

A N balance for the proposed municipal wastewater treatment system is depicted in Figure 3. A typical raw municipal wastewater contains about 30-50 mg/l total Kjeldahl nitrogen (TKN) (Metcalf and Eddy, 2003). Settled sludge in the primary clarifier solids is approximately 0.5-1% of the influent flow with 2-7% solids, with approximately 1.5-4% of those solids consisting of N (Metcalf and Eddy, 2003; Turovskiy and Mathai, 2006). Using 4% total solids for the primary sludge and 2.5% N in the solids, N content was calculated (Metcalf and Eddy, 2003; Turovskiy and Mathai, 2006). Approximately 10% of AnMBR’s influent N is removed in the solids through biomass growth (Grundestam and Hellstrom, 2007). Flow rate of the AnMBR waste solids was estimated in accordance with Kim *et al.* (2011): 4.4 hr hydraulic retention time and 50 day solids retention time. In solids handling, dewatering with a belt filter press results in approximately 85% solids capture; these solids contain approximately 3.3% N (Metcalf and Eddy, 2003). By solving a system of equations for solids dewatering, the flow rate for solids and supernatant as well as the supernatant N concentration were calculated. As shown in

Figure 3, theoretically 7% of N is removed in biosolids, 10% of influent N is in the solids dewatering supernatant leaving and 93% of influent N is in the final effluent if the solids dewatering supernatant is recycled to the primary clarifier.

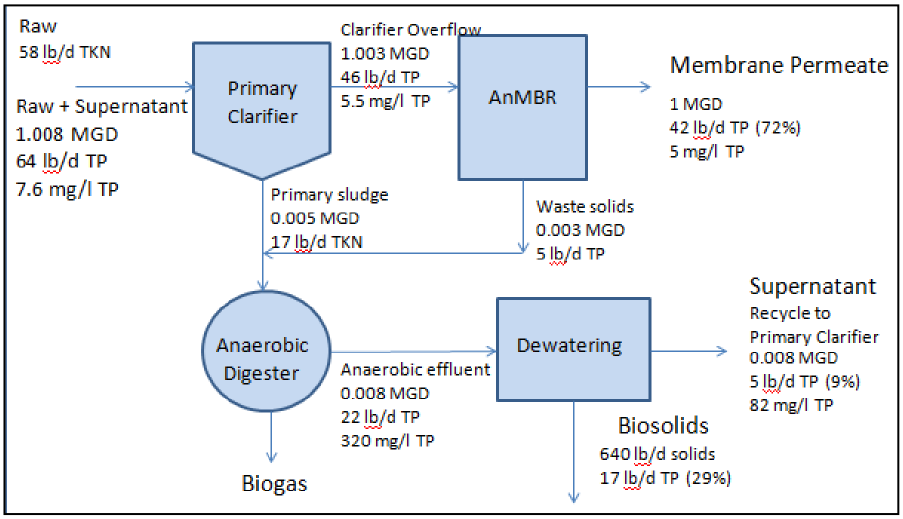

Figure 4: Estimated P balance for 1 MGD anaerobically treated municipal wastewater

A P balance was completed for an AnMBR treatment plant and is depicted in Figure 4. Influent total phosphorus (TP) averages about 4-12 mg/l (Metcalf and Eddy, 2003). P content in the primary sludge solids is about 1%; primary sludge P content in Figure 4 was calculated with the previously stated solids content (Metcalf and Eddy, 2003). An AnMBR is estimated to remove about 10% TP through biological growth and particulate reject by the membrane (Grundestam and Hellstrom, 2007). Therefore the final effluent TP concentration would be 3.5 mg/l TP. In the biosolids from dewatering of anaerobic digester effluent, there is about 0.9 to 5.2% TP (European Commission, 2001). Since dewatered solids supernatant typically contains 60 mg/l TP or greater, a TP concentration in the biosolids of 1.5% was used for calculations (Forrest et al., 2008). Figure 4 shows that 50% of the influent P can be recovered in the biosolids, 11% could be recovered in the sludge dewatering supernatant and 50% in the final effluent if the supernatant is recycled.

1.2 Recovery Streams Review

Selection of an applicable technology for nutrient recovery is highly dependent upon the characteristics of the wastewater to be treated. In this study, AnMBR permeate or SDS was targeted for nutrient recovery. Anaerobic digester SDS has been well characterized and studied for nutrient removal and recovery. This stream typically contains ammonium-N (NH_4-N) and PO_4-P concentrations of 600 and 70 mg/l, respectively (USEPA, 1979). Since it is the liquid stream from solids digestion and dewatering, there is also a significant 5-day BOD (BOD_5) and TSS associated with the stream, 100-2,000 and 100-10,000 mg/l, respectively (USEPA, 1987). Struvite precipitation has been widely investigated in this stream and is now being applied full-scale with companies such as Ostara and Multiform Harvest (Clean Water Services, 2013; Ostara, 2013). Precipitation of struvite recovers most of the PO_4-P and a portion of N from the sidestream (Munch and Barr, 2001). Another technology developed for this stream is partial nitritation and Anammox. This process simply removes N, but does so with less carbon and energy than nitrification/denitrification (van Dongen *et al.*, 2001).

Full-scale AnMBR has not been well defined since much of the work with these systems has been at pilot and lab scale with little or no full-scale municipal wastewater implementation (Smith *et al.*, 2012). AnMBR are capable of producing permeate with effluent COD and TSS of less than 80 and 1 mg/l, respectively; effluent COD in one process was 7 mg/l (Gimenez *et al.*, 2011; Kim *et al.*, 2011; Martinez-Sosa *et al.*, 2011). A submerged AnMBR treating screened raw sewage produced an effluent with 33 mg/l NH_4-N, 3.1 mg/l PO_4-P, 95 mg/l S^{2-}, and 1.7 mg/l SO_4-S (Gimenez *et al.*, 2011). Influent NH_4-N and PO_4-P concentration were less than effluent concentrations in the Gimenez *et al.* (2011) system, suggesting that PO_4-P was being released by microbes and organic N undergoes ammonification in the anaerobic reactor. In the work of Gimenez *et al.* (2011), influent sulfur was in the sulfate form and most of it was reduced to sulfide with a small amount lost to gas and less than 2% remaining as sulfate. TP and TKN concentrations in an AnMBR were reduced by 9% each during a study by Grundestam and Hellstrom (2007). Therefore, it was estimated that only about 9% of nutrients will be removed through biological uptake and membrane rejection. Since there is no mechanism for removal and because the dissolved constituents will pass through the membrane, little change in the concentration of NH_4^+, PO_4^{-3}, ionic sulfur (SO_4^{-2}+S^{2-}), Ca^{2+}, Mg^{2+}, K^+, bicarbonate (HCO_3^-), and Cl^- is expected. However, the amount of organics and solids will be significantly reduced. AnMBR permeate should contain few organic nutrients due to membrane rejection and ammonification. An extra step for nutrient removal and/or recovery is needed following anaerobic secondary treatment.

1.3 Nutrient Removal Review

A review of nutrient removal and recovery technologies was conducted in order to develop a recovery process to be tested in the lab and to perform an initial removal process comparison. The selected removal and recovery processes were to fit into the treatment train depicted in Figure 2. The objective of the review was to assess the characteristics of each N and P removal technology and compare them based on the project goals. The priority goals for selecting a treatment process were as follows: value of recoverable, footprint, treatment capability, energy and chemical use, and degree of development. Treatment capability encompasses influent wastewater characteristics suitable for the process and effluent quality. Wastewater characteristics into a unit process were estimated based upon the mass balances in Figures 3 and 4. Processes were categorized as biological or chemical/physical processes and removal or recovery processes. Text books, peer-reviewed journal articles, presentations, and other sources were used to collect information on nutrient removal processes. A complete list of the technologies discussed in the following sections and their recoverables can be found in Tables A1 and A2 for N and P, respectively.

1.31 Suspended Growth Biological Nitrogen Removal

Organisms used for biological treatment nutrient removal can be subdivided into heterotrophic or autotrophic organisms and the organisms may grow either attached or in suspension. Suspended growth microbes are typically used for municipal wastewater treatment. N is removed through an aerated tank in which microbes nitrify NH_4^+ into nitrite (NO_2^-) and nitrate (NO_3^-). In a second tank that is anoxic, microbes convert NO_2^- and NO_3^- into N_2. This process is known as nitrification/denitrification. Instead of a two reactor system, there are many other potential configurations, including a sequencing batch reactor, oxidation, Modified Ludzack-Ettinger, 4-Stage Bardenpho, and simultaneous nitrification/denitrification (SNdN) (USEPA, 2010). In a sequencing batch reactor, the wastewater enters the tank, is aerated to nitrify then allowed to become anoxic to denitrify (USEPA, 1993). The wastewater is then discharged. An oxidation ditch is a large oval with aerobic and anoxic zones (Metcalf and Eddy, 2003). Modified Ludzack-Ettinger and the 4-Stage Bardenpho processes involve arrangement of multiple oxic and anoxic tanks (Metcalf and Eddy, 2003). SNdN occurs when the DO concentration is low enough that oxygen does not reach all microbes in flocs (USEPA, 2010). With these suspended growth methods, most of the N is lost to the atmosphere, but some is recovered in the wasted biosolids as organic N (Metcalf and Eddy, 2003).

A suspended growth process that can be used in concentrated NH_4^+ streams is the **S**ingle reactor system for **H**igh activity **A**mmonium **R**emoval **O**ver **N**itrite (SHARON) with denitritation or Anammox. This reactor operates at a high temperature (30-40 °C) with equal hydraulic retention time and solids retention time (van Dongen et al., 2001). If denitritation, the conversion of nitrite to N_2, is next in the process then all NH_4^+ is converted to NO_2^- without conversion of NO_2^- to NO_3^-, therefore reducing energy requirements. If Anammox microbes are utilized in the second reactor, then half of the NH_4^+ is converted to NO_2^- in the SHARON reactor and in the Anammox tank NO_2^- and NH_4^+ are converted to N_2 (van Loosdrecht et al., 2009). This saves aeration needed to nitrify NH_4^+ and reduces the carbon requirements in the anoxic tank since NH_4^+ acts as the electron donor (van Dongen et al., 2001). A recently developed process, **C**ompletely **A**utotrophic **N**itrogen-removal **O**ver **N**itrite (CANON), combines SHARON and Anammox in one tank. In this reactor NH_4^+-oxidizing bacteria outgrow nitrite-oxidizing bacteria and cooperate with Anammox bacteria (Zhang et al., 2012). SHARON-Anammox and CANON have not been operated for mainstream wastewater treatment.

SHARON has been operated full-scale in the Netherlands and Anammox reactors have been operated full-scale in the Netherlands, Japan, China, Poland, and UK (Ni and Zhang, 2013). Full-scale CANON facilities can be found in the Netherlands, Switzerland and China (Haandel and Lubbe, 2012).

1.32 Attached Growth Biological Nitrogen Removal

Attached growth processes have been developed to increase microbial contact with wastewater, thereby reducing the footprint required. These processes still require an aerobic and anoxic zone for nitrification and denitrification. Common attached growth reactors include: biological aerated filter (BAF), fluidized bed bioreactor (FBBR), moving bed biofilm reactor (MBBR), rotating biological contactor (RBC), and trickling filter (TF). In a BAF, the bed is packed with a media such as plastic and the wastewater is passed either down or up through the bed (Canler and Perret, 1994). In FBBRs and MBBRs media is suspended, but an FBBR is a column shape with wastewater fed upwards to fluidize the media while an MBBR tank has a rectangular surface area with air or a mixer to keep the media suspended and moving (Metcalf and Eddy, 2003; USEPA, 2010). Rotating biological contactors are large rotating disks that provide oxygen to bacteria when exposed to air then are re-submerged in the wastewater through a continuous cycle. Trickling filters consist of a large surface area tank with rocks or plastic through which wastewater is allowed to flow by gravity (Daigger and Boltz, 2011). The MBBR and RBC have been used for full-scale secondary treatment of wastewater; however, the other attached growth processes are designed for tertiary treatment (Metcalf and Eddy, 2003). N can be recovered from the backwash of TFs, BAFs, and FBBRs through solids dewatering and land application of biosolids; however, most of the N is lost to the atmosphere.

1.33 Photosynthetic Biological Nitrogen Removal

Nutrient removal can be accomplished through an algae or floating aquatic organism pond and algae reactors (Singh and Thomas, 2012; USEPA, 1993; van der Steen *et al.*, 1999). With these ponds, N and P are taken up in the biomass and the ponds also contain microorganisms capable of nitrification/denitrification. Suspended organic P can be settled in the ponds. This method requires a large footprint and has poor treatment efficiency at low temperatures (USEPA, 1980). The biomass can be harvested if a cost-effective technique for algae separation from water is available (Cai *et al.*, 2013). Novel algae reactor designs have been developed to minimize footprint and increase the ability to harvest biomass. These include the following: high rate algal pond (HRAP), tubular photobioreactor, membrane algae bioreactor, and the Algaewheel. Tubular photobioreactors allow for more light penetration into the algae biomass, but can overheat, accumulate toxic concentrations of O_2 and have a high initial investment costs (Arbib et al., 2013). Although HRAPs are easier to operate than closed systems, there is poor mixing, a large area requirement, and high diffusion rates to the atmosphere (Arbib et al., 2013). Membrane bioreactors with algae cultivation can be used for tertiary nutrient removal (Singh and Thomas, 2012). Utilizing membranes allows for algae retention and therefore a more rapid rate of nutrient removal. It also increases the concentration of algae, making biomass recovery more efficient. The Algaewheel is capable of removing nutrients and BOD and includes a spool harvesting technique for algae separation from water (Christenson and Sims, 2012). During the spool harvesting technique, cord lining a rotating algae wheel is passed through a scraper to detach biomass and then is wound back onto the wheel (Christenson and Sims, 2012).

1.34 Biological Phosphorus Removal

P can be removed through biological uptake in a process known as biological phosphorus removal (BPR). This process utilizes a specific group of microorganisms known as PO_4-P accumulating organisms (PAOs) that take up more PO_4-P than typically found within microbial cells (Metcalf and Eddy, 2003). During anaerobic conditions, PAOs release polyphosphate and uptake readily biodegradable compounds, typically short-chain volatile fatty acids (VFA) (USEPA, 2010). Under aerobic conditions, the microorganisms use energy from the VFAs stored as poly-β-hydroxy-alkonates to uptake P into their cells (USEPA, 2010). These organisms have a competitive advantage in sequential anaerobic-aerobic environments with high substrate (i.e., VFA) concentration in the anaerobic period in that they can store energy where as other microorganisms must wait for oxygen to be present to uptake VFAs (USEPA, 2010). The steps to BPR are as follows: anaerobic zone for VFA uptake, aerobic zone for P uptake and cell growth, and clarification to settle PAO for waste and recycle (Metcalf and Eddy, 2003). P removal is improved since organisms containing excess PO_4-P are wasted for solids handling. Suggested wastewater constituent ratios for effective BPR performance, include the following: BOD:TP=20:1, readily biodegradable chemical oxygen demand (rbCOD) to TP ratio of 10-16:1 and VFA:TP=4-16:1 (Barnard *et al.*, 2006; Neethling *et al.*, 2005;

WEF and ASCE, 2006). Carbon sources may come from the wastewater, a process may be added to ferment the waste, or external sources of carbon, such as molasses, may be added (USEPA, 2010).

1.35 Physical/Chemical Nitrogen Removal

The physical/chemical technologies for removing or concentrating NH_4^+ from wastewater include the following: breakpoint chlorination, ion exchange (IX), and electrodialysis. Ion exchange using zeolite has been studied for NH_4^+ removal for 80 years (Gleason and Loonam, 1933). As wastewater passes through the IX column containing zeolite, NH_4^+ is attached to the zeolite surface in exchange for Na^+ or other cations. With this media treating municipal wastewater, the NH_4-N effluent concentration is typically less than 1 mg/l for around 130 bed volumes treated (USEPA, 1993). Regeneration of the IX column with a high pH salt produces high NH_4-N concentration salt water. Electrodialysis is a method for concentrating NH_4^+ ions by applying a current to a selective membrane, causing the ions to pass from the sample to a concentrated solution on the other side of the membrane (Ippersiel *et al.*, 2012). The benefit of concentration with electrodialysis or IX is that it provides a concentrated solution more suitable for recovery technologies. Breakpoint chlorination is the addition of chlorine to the point at which NH_4^+ is oxidized to N_2 (USEPA, 1980). Breakpoint chlorination can result in chlorinated organics formation and is not recommended for total N removal (USEPA, 1993).

NH_4^+ can be removed and recovered from wastewater through physical/chemical methods such as ammonia transfer to the gas phase with subsequent absorption or struvite precipitation. Air stripping, vacuum distillation, and vacuum membrane distillation all work by the same mechanism: ammonia conversion to the gas phase. This is accomplished by adjusting the pH to 10.8 or greater and then forcing ammonia into the gas phase by passing it countercurrent to air in a packed bed tower (air stripping), spraying the liquid into drops in a vacuumed tank (vacuum distillation), or passing the solution through a membrane allowing only gas transfer (vacuum membrane distillation) (El-Bourawi *et al.*, 2007). The ammonia gas must then be captured in acidic water, carbonic acid, nitric acid, or sulfuric acid. The final technology is struvite precipitation. Struvite is a slow-release fertilizer with the chemical formula $MgNH_4PO_4$. This process has been developed at full-scale to treat high NH_4-N concentration streams such as the SDS; however, mainstream recovery work has been limited. This process requires the addition of a Mg^{2+} source such as $MgCl_2$ and pH adjustment to around 8-10 depending on wastewater composition for maximum struvite precipitation (Adnan *et al.*, 2003).

1.36 Physical/Chemical Phosphorus Removal

Removal of P by physical/chemical methods includes precipitation with a metal salt, ballasted flocculation, electrodialysis, adsorptive filtration, ion exchange, thermal-metallurgical recovery, and wet chemical extraction. Precipitation of PO_4-P by metal salts, typically ferric chloride (ferric) or aluminum sulfate (alum) is a widely accepted and utilized practice in wastewater treatment (USEPA, 2000b). This process is effective; however, excess ferric or alum is required due to competing chemical reactions (USEPA, 2000b). Polyaluminum chloride is another metal salt that can be utilized for P removal. Polyaluminum chloride can also be used to increase remove organics and suspended solids; in addition it can decrease irreversible fouling rate when added to membrane bioreactors (Gasiunas and Askinis, 2011; Teli *et al.*, 2012). P removal is also possible through magnetite seeded calcium PO_4-P precipitation (Karapinar *et al.*, 2004). Removal of PO_4-P by precipitation occurs through formation of super-saturation, nucleation and crystal growth (Karapinar *et al.*, 2006). Struvite precipitation, as described previously with respect to N, is effective for P removal as well. P is typically the limiting nutrient as P is found in insufficient quantities to remove all N when precipitating struvite in municipal SDS or anaerobically digested dairy manure (Munch and Barr, 2001). The product is valuable as a slow-release fertilizer (Yilmazel and Demirer, 2011).

P can be captured and concentrated in a liquid stream through adsorption/desorption, ion exchange, or electrodialysis. There are a number of adsorbents for PO_4-P, including: iron-based adsorbents, poly hydrogels, adsorbent beads (Ashahi Kasei Chemical, Tokyo, Japan), titanium dioxide, raw dolomite, iron and manganese mixtures, steel slag, blast-furnace slag, coal slag, red mud, iron-oxide tailings, and aluminum oxide (Rittman *et al*., 2011). Iron-oxide coated sand filtration has been developed to selectively remove PO_4-P and suspended solids. The media is continually sheared of PO_4-P and new iron coating is added. This process has been proven to provide effluent TP of less than 0.075 mg/l as tertiary municipal wastewater treatment (Newcombe *et al.*, 2008). Ion exchange of PO_4-P is a method that can concentrate PO_4-P, similar to adsorption. As with NH_4^+ IX, an ion on the media surface is transferred into solution with PO_4-P taking its place on the media surface. Currently well-researched exchange materials include metal-loaded chelating resins, hydrotalcites, iron-based hydroxide compounds and capacitive deionization (CD) on electrodes (Rittmann *et al.*.

2011). PO_4-P ions accumulate on oppositely charged carbon electrodes in CD. Metal-loaded resins have shown a high selectivity towards PO_4-P and the ability to be regenerated at greater than 95% recovery of exchanged PO_4-P (Sengupta and Pandit, 2011).

In some locations, wastewater sludge are incinerated due to regulations against landfilling, the high cost of landfilling, or other factors. However, this sludge is rich in P and many technologies have been developed to capture this P either through wet chemical extraction or thermal metallurgical recovery (Rittmann *et al.*, 2011). During thermal metallurgical recovery, sewage sludge ash is mixed with a chloride (Cl^-) donor and then heated to greater than 750 °C (Adam *et al.*, 2009). This removes metal chlorides from the ash and provides a highly bioavailable P ash, but these metal chloride gases must then be treated (Adam *et al.*, 2009). Wet chemical treatment of sewage sludge ash decreases the ash pH to leach metals and PO_4-P followed by two steps for separation of heavy metals and P from the acidic water (Takashashi *et al.*, 2001). There are many different variations of this technology on the market as described by Rittmann *et al.* (2011).

1.4 Nutrient Recovery Scheme

A multi-step process for nutrient recovery was developed based on the literature review. Ion exchange was selected for both PO_4-P and NH_4^+ as a way to concentrate the N and P. Selection of IX was based upon treatment of wastewater with nearly no solids and low BOD; solids will cause plugging in IX columns and elevated BOD can cause biological fouling of the media. In addition, the recovery technologies are less expensive to operate in concentrated streams; therefore, IX can be used as a lower-cost method to produce concentrated N and P streams. Struvite precipitation was selected as the method for removing PO_4-P and a portion of the NH_4^+ as the recovered product can be used as a fertilizer (Forrest *et al.*, 2008). Since there is not enough P to remove all N through struvite precipitation, vacuum ammonia distillation and absorption was selected to recover N from the remaining concentrated N stream. Ammonia gas stripping and absorption is the only technology well-developed for complete recovery of aqueous NH_4^+. Vacuum distillation is the preferred method of gas transfer since the energy requirements and tank space are less than that of traditional gas stripping towers (Orentlicher *et al.*, 2007).

The system developed for NH_4^+ and PO_4^{-3} recovery is depicted in Figure 5. Removal of P in the HPO_4^{-2} and $H_2PO_4^-$ form by anionic IX was investigated herein. NH_4-N removal using IX with clinoptilolite was also investigated. Regeneration eluate from anion exchange containing a high concentration of PO_4-P and a fraction of the cation regenerant containing high NH_4-N concentration are combined in a flask with magnesium addition in order to precipitate struvite. Effluent from the struvite reactor could be recycled for PO_4-P IX regeneration. Recovery of NH_4^+ from the regeneration eluate could be performed using vacuum distillation at pH of around 11. Ammonia gas from the distillation process could be absorbed in an acid such as sulfuric acid to create $(NH_4)_2SO_4$ solution. Reduced ammonia wastewater from the vacuum distillation process could be recycled for use as the regenerant at the end of each IX cycle.

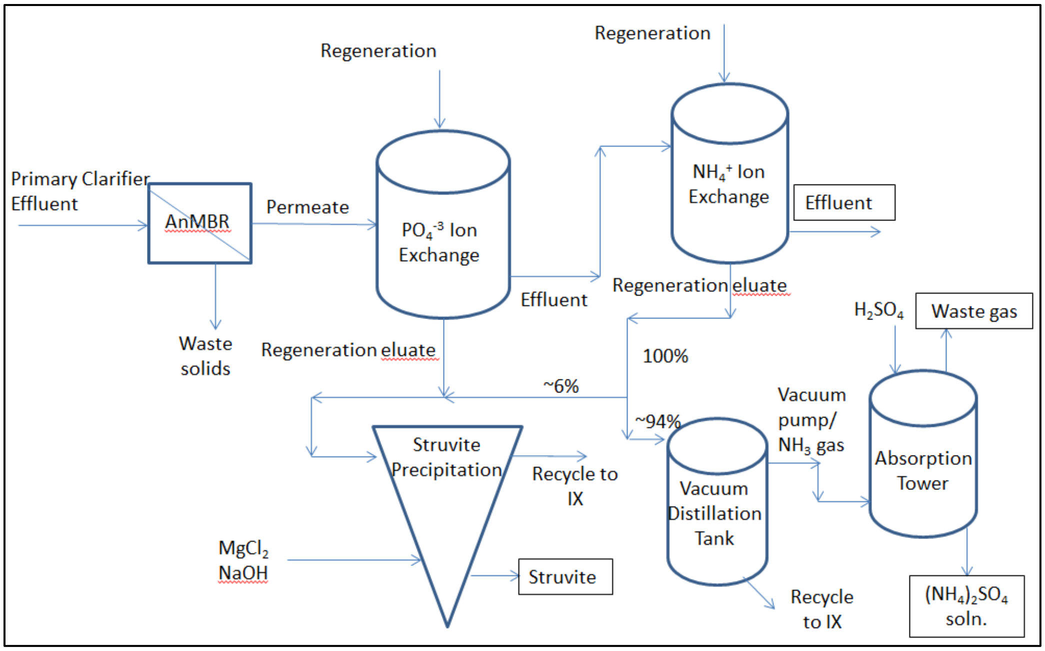

Figure 5: Nutrient recovery schematic

1.5 Ion Exchange Physico-chemistry

Ion exchange is the process of transfer of an ion on a solid surface for a similarly charged ion in solution. This exchange occurs in equivalent amounts of charge and is reversible (Reynolds and Richards, 1996). For example one Ca^{2+} ion in solution will transfer to the solid phase in exchange for two Na^+ ions. This Ca^{2+} ion would be bonded to the same surface sites as the two Na^+ ions were originally. The total exchange capacity is measured as equivalents per g or L of solid: in other words, the number of equivalents of exchangeable ions per unit of media. An exchange preference for ions exists for each media and is dependent upon surface functional groups and characteristics of the material (Eckenfelder, Jr. *et al.*, 2009). For example, a media such as zeolite with Na^+ ions on the surface will exchange with different amounts of K^+, Ca^{2+}, Mg^{2+}, and NH_4^+. Some of the important factors in determining exchange amount and rate include the following: size and valence of ions being exchanged, concentration of ions in solution, physical/chemical nature of media, and temperature (Eckenfelder, Jr. *et al.*, 2009). There are synthetic and natural ion exchangers; natural ion exchangers include materials such as zeolites and clays while synthetic exchange resins are polymers containing reactive surface groups (Reynolds and Richards, 1996). Synthetic resins are either cationic or anionic depending on the surface group. In water and wastewater treatment, IX is used for removal of hardness, metals, and nutrients (Weber, Jr., 1972). In an operating column, media will produce a consistent effluent until exchange capacity begins to be exhausted; at this point the effluent concentration of the targeted ion will begin to increase until it becomes equal to the influent. Flowrate in IX systems is typically 1 to 8 gpm/ft^2; the height-to-diameter ratio should be about 1.5:1-3:1 (Reynolds and Richards, 1996). When the media is exhausted, it is typically backwashed and then regenerated by passing a 5-10% brine solution through the column. Backwashing will result in bed expansion of 75-100% in synthetic resins and 25% in zeolites; therefore, tanks must be designed to handle this increase in volume (Reynolds and Richards, 1996). This forms a concentrated solution of the ion exchanged during the service cycle. Valuable heavy metals and other compounds can be recovered from this regenerant stream. Finally there is a rinse cycle prior to starting the next service cycle (Weber, 1972).

1.6 Ammonium Ion Exchange

Removal of NH_4^+ from wastewater by IX was first researched in the early-to-mid 1900's (Gleason and Loonam, 1933). The media typically used for NH_4^+ ion exchange is clinoptilolite, a natural mineral which is a type of zeolite (USEPA, 1980). Exchange of ions occurs in minerals between two layers of either silica-oxide or alumina-oxide tetrahedral in which there is a deficit of positive ions (Reynolds and Richards, 1996). At this location, cations such as K^+, Ca^{2+}, Mg^{2+}, etc. are weakly bonded to the surface and will exchange with ions in solution based on a chemical potential (Kitsopoulos, 1999). Despite the mineral's lower total exchange capacity in comparison to synthetic resins, zeolite's selectivity for NH_4^+ compensates for the exchange deficiency (Koon and Kaufman, 1975). Potassium is the only ion clinoptilolite is more selective towards than NH_4^+ (USEPA, 1993). Exchange capacity of the clinoptilolite in wastewater applications is about 0.2-0.5 meq/L (USEPA, 1993). This process is not significantly affected by temperature and can reduce influent NH_4-N concentrations of 10-50 mg/l to within the range of 0.2 to 3 mg/l (USEPA, 1980). With typical wastewater NH_4-N concentration, about 25-30 mg/l, zeolite can reduce NH_4-N to less than 1 mg/l in about 130 bed volumes (BV) of wastewater (Cooney and Booker, 1999; USEPA, 1993).

Once the IX bed is exhausted, the media must be regenerated. Regeneration of clinoptilolite is accomplished using 10-20 BV of a high pH salt solution (USEPA, 1993). High pH salt solutions may include an individual chemical or some combination of NaCl, NaOH, and/or $Ca(OH)_2$. Calcium hydroxide solution is suggested by Metcalf and Eddy (2003). Using $Ca(OH)_2$ may be beneficial if ammonia is to be stripped from the regenerant as it reduces the need for chemicals in the next step since the pH is already elevated above 11; however, Ca^{2+} will not exchange from the surface as easily as Na^+ (Hedstrom, 2001). Previous work has utilized NaCl concentrations at an elevated pH to increase the speed of regeneration (Hedstrom, 2001). Guo *et al.* (2013) looked at the optimal regenerant salt and NaOH concentration and determined that 2% NaCl with 0.1 M NaOH was sufficient; however, this test was performed with treatment of high NH_4^+ wastewater which may affect the IX-regeneration characteristics. There is a point at which the pH becomes too excessive as it causes attrition of the zeolite; however, this point is not defined (Koon and Kaufmann, 1975). Peak regenerant concentration is around 500 mg/l NH_4-N when treating municipal wastewater and desorbing NH_4^+ with NaCl at an elevated pH (Cooney and Booker, 1999; Du *et al.*, 2005). Zeolite has been shown to maintain exchange capacity after 12 IX cycles utilizing a 3.5% NaCl solution at a pH of 10; testing ended after 12 cycles (Cooney and Booker, 1999).

Operational risks to consider include plugging, biological fouling, inorganic fouling, and reduction in exchange capacity. Excess solids pose the threat of plugging the IX column, causing an increase in pressure drop and reduction in exchange capacity. Typically regeneration is preceded by backwashing to remove solids; however, in the current study's system nearly no solids will be present due to membrane rejection in the AnMBR. There is the potential for biological fouling due to the concentration of organics and inorganic fouling caused by precipitation of calcium or magnesium hydroxides. However, biological fouling risks would appear to be limited due to the low BOD and high pH regenerant. The Langelier Saturation Index is calculated using Equations 1 and 2 to estimate the inorganic fouling potential of the wastewater (Langlier, 1936).

$pH_{sat} = -log\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} - (-\log\{[Ca^{2+}][CO_3^{2-}]\}) - \log[Ca^{2+}] - \log[ak]$ Equation (1)

Where,

$[H^+]$= Concentration of H^+ (mol/L)

$[CO_3^{2-}]$= Concentration of CO_3^{2-} (mol/L)

$[HCO_3^-]$= Concentration of HCO_3^- (mol/L)

[ak]= Alkalinity of wastewater (mol/L)

$LSI = pH_{actual} - pH_{sat}$ Equation (2)

Where,

LSI=Langelier Saturation Index

pH_{actual}=pH of wastewater

Calculated LSI values less than 1 indicate slight to moderate fouling potential, 1 to 3 indicates strong to very strong fouling potential, and greater than 3 is severe fouling potential (Cremaschi *et al.*, 2012). Results for the wastewater used in this study will be described in the section, Wastewater Characterization.

Cations in solution will affect the uptake of NH_4^+; in municipal wastewater the cations found in significant concentrations are K^+, Na^+, Mg^{2+}, Ca^{2+}, and Al^{3+}. Uptake of these ions with clinoptilolite has been studied in tertiary treated wastewater, urine and stored urine, and concentrated NH_4^+ streams (Beler Baykal *et al.*, 2009; Cooney and Booker, 1999; Guo *et al.*, 2013). In one study, tertiary treated wastewater contained 12, 10, and 15 mg/l Ca^{2+}, Mg^{2+}, and K^+, respectively (Cooney and Booker, 1999). Potassium concentrations are similar to expectations for AnMBR permeate; however, Mg^{2+} and Ca^{2+} are expected to be closer to 35 and 70 mg/l, respectively based on conventional primary effluent (Metcalf and Eddy, 2003). Magnesium breakthrough occurred at about the same time as NH_4^+; K^+ and Ca^{2+} never had complete breakthrough as a result of preferential exchange (Cooney and Booker, 1999). Peak regenerant concentrations of K^+, Ca^{2+}, and Mg^{2+} were about 300, 270, and 170 mg/l, respectively; (Cooney and Booker, 1999). The greater the salt concentration, the greater efficiency of K^+ desorption (Guo *et al.*, 2013). NH_4-N and K^+ exchange were similar between IX cycles, with K^+ being slightly greater after cycle 1 (Guo *et al.*, 2013). Weatherley and Miladinovic (2004) showed that the presence of K^+, Ca^{2+}, and Mg^{2+} decreased NH_4^+ removal, but not significantly. Removal of NH_4^+ decreases in the presence of other cations due to their occupation of exchange sites.

1.7 Phosphate Ion Exchange Review

PO_4^{-3} can be removed from wastewater using IX just as discussed with NH_4^+; however, synthetic resins are typically used for PO_4-P removal. This process has been researched for PO_4-P removal due to its ability to work in variable wastewater composition, flow-rate and temperature; however, the challenges associated with PO_4-P IX include the following: poor selectivity towards PO_4-P over other ions, inefficient regeneration, and loss of loading capacity due to fouling (Petruzzelli *et al.*, 2003). Despite these challenges, the process could be optimized to overcome these three issues. Selectivity towards PO_4-P can be enhanced by loading resins with iron, copper, or other metals that form a strong coordination bond with HPO_4^{-2} and $H_2PO_4^-$ (Sengupta and Pandit, 2011). Typical resins used as the base for loading with metal, include Dow M4195 and Dow 3N (Petruzzelli *et al.*, 2003; Sengupta and Pandit, 2011). Biological and inorganic fouling issues should be minimized by treating AnMBR permeate that contains a low concentration of BOD_5 and organics. With many different resins to choose from, efficiency of regeneration could be optimized by testing various media with multiple regenerants. Regenerant could be beneficially used to recover PO_4-P: thereby providing a valuable product to offset process costs. Previous work has been performed using PO_4-P IX with struvite precipitation of the regenerant (Sengupta and Pandit, 2011). Zeolite regenerant has been proposed as a N or K source in struvite precipitation of this process (Petruzzelli *et al.*, 2003). A patent on selective IX of N, K, and P with struvite recovery from the regeneration eluates is held by Liberti *et al.* (1984).

A list of PO_4-P selective resins from the literature is shown in Table 1. Resins that selectively remove PO_4-P are either polymeric ligand exchange resins, impregnated with metal nanoparticles, or a combination thereof (Sengupta and Pandit, 2011). Polymeric ligand exchange resins attract Lewis bases such as PO_4-P (Zhao and Sengupta, 1998). Zhao and Sengupta (1996) first developed copper loaded resin that was prepared by passing 1N HCl, 1N NaOH, and then 500 mg/l Cu^{2+} solution at a pH of 4.5 through the resin until saturation; the resin was considered saturated when effluent Cu^{2+} was equal to influent; this resin was patented in 2000 (Sengupta *et al.*, 2000; Zhao and Sengupta, 1998). The resin, Dow-Cu, was shown to treat just over 1,000 bed volumes (BVs) of wastewater containing concentrations of 4 mg/l P, 56 mg/l HCO_3^-, 100 mg/l SO_4^{-2}, 71 mg/l Cl^-, and 93 mg/l NO_3^- (Zhao and Sengupta, 1998). However, using secondary effluent that contained total organic carbon (TOC), resin breakthrough occurred at about 700 BV with 2.2 mg/l P in the influent. Zhao and Sengupta (1998) recovered 96% of PO_4-P from Dow-Cu in the regenerant within 8 BV using 6% NaCl (pH=4.3). This resin was then used in a pilot plant by Petruzzelli *et al.* (2003). The pilot IX column was treating secondary effluent with a P concentration of 4 mg/l; the column successfully removed PO_4-P for 150 BV at a flow rate of 10 BV/h. Regeneration was successful in concentrating P 130 times using the chemical mix from Table 1; a total of 3 BV regenerant was required (Petruzzelli *et al.*, 2003). Performance of the copper-loaded resin decreased by 10-15% after 3 months of continuous operation (Petruzzelli *et al.*, 2004).

Table 1: Phosphate selective IX resin literature

Citation	Media	Experiments	Sample	Regenerant
Blaney *et al.*, 2007	HAIX	Column, regeneration	Synthetic, secondary wastewater	2% NaCl + 2% NaOH
Kumar *et al.*, 2007	Dow-Cu & HAIX	Column, regeneration	Synthetic, Membrane bioreactor RO concentrate	6% NaCl, pH=4.3
Martin *et al.*, 2009	HAIX	Column, regeneration	Final effluent w/ precipitation or w/ trickling filter	2% NaCl + 4% NaOH
Martin *et al.*, 2013	HAIX	Column	Final effluent w/ trickling filter, groundwater + P	N/A
O' Neal and Boyer, 2013	HAIX	Batch, regeneration	Synthetic, urine, diluted urine	2% NaCl + 2% NaOH
Pan *et al.*, 2009	HFO-201	Batch, column, regeneration	Synthetic, pesticide-mfg effluent	5% NaOH + 5% NaCl
Petruzzelli *et al.*, 2003	Dow-Cu	Column, regeneration	Synthetic	1 M NaCl, pH=4.3
Sendrowski and Boyer, 2013	HAIX	Batch	Urine and hydrolyzed urine	N/A
Sengputa and Pandit, 2011	HAIX, Dow-HFO, & Dow-HFO-Cu	Batch, column, regeneration	Synthetic	2.5% NaCl + 2% NaOH
Wu *et al.*, 2007	Lanthanum loaded resin	Column, regeneration	Synthetic, seawater	6 M NaOH or 6 M NaCl
Zhao and Zengupta, 1996	Dow-Cu	Column, regeneration	Secondary wastewater	6% NaCl, pH=4.3
Zhao and Sengupta, 1998	Dow-Cu	Batch, column, regeneration	Secondary wastewater	6% NaCl, pH=4.3
Zhu and Jyo, 2005	Zirconium loaded resin	Column, regeneration	Synthetic, river water, seawater	0.5 M NaOH

Four types of resin loaded with iron have been reported in the literature: HFO-201, hydrated ferric oxide (HFO) impregnated resin (DOW-HFO) and hybrid anion exchanger (HAIX) which is also known as LayneRT™, and Cu^{2+} loaded and HFO impregnated resin (DOW-HFO-Cu). DOW-HFO is prepared by adding 10 g of virgin resin to 1 L of solution containing 2 g/L Fe in the form of $FeCl_3*6H_2O$; this resin was patented in 2007 (Sengupta *et al.*, 2007; Sengupta and Pandit, 2011). The resin is mixed for 1 hr, stepwise increased in pH to 8 over 3 hr by 1N NaOH and then slowly mixed for 24 hrs; finally the resin is rinsed multiple times and dried for 24 hr at 45 °C (Sengupta and Pandit, 2011). LayneRT™ is available commercially through Layne Christensen Company (The Woodlands, TX). In tests run with reverse osmosis (RO) concentrate containing 12 mg/l P, breakthrough of LayneRT™ and Dow-Cu resin occurred after about 200 and 40 BV, respectively (Kumar *et al.*, 2007). Work by Martin *et al.* (2009) showed that LayneRT™ was only capable of treating 10 BV to an effluent P concentration of less than 0.1 mg/l when the influent wastewater contained 4.7 mg/l P. This may be a result of the excess concentration of nitrate, 157 mg/l, and other ions (Martin *et al.*, 2009). However, in later work by Martin *et al.* (2013), the resin was more effective as column size increased, treating 675 BV of 4.7 mg/l P wastewater to less than 0.1 mg/l P. In recent work by Sengupta and Pandit (2011), a resin loaded with an Fe and Cu (DOW-HFO-Cu) method, was observed to treat about twice as much wastewater as the LayneRT™ resin with the same level of removal efficiency. In this study, the LayneRT™ column treated about 625 BV of water containing P and SO_4^{-2} concentrations of 2.75 and 20 mg/l, respectively (Sengupta and Pandit, 2011). Regeneration of LayneRT™ was accomplished in less than 10 BV, while it required almost 15 BV to regenerate DOW-HFO-Cu (Sengputa and Pandit, 2011).

1.8 Struvite Precipitation Review

Precipitation of NH_4^+ and PO_4^{-3} is possible with the addition of magnesium to form struvite pellets. Struvite is solid magnesium ammonium phosphate ($MgNH_4PO_4$). This chemical is formed in equimolar amounts of P and N; this ratio is equivalent to 14 mg/l NH_4-N for 31 mg/l PO_4-P. The two parameters most critical to struvite precipitation are the molar ratio of Mg:P:N and the pH (Britton *et al.*, 2005). A parameter that accounts for pH and ion concentrations is the supersaturation ratio (SSR), which describes the mixture of wastewater, $MgCl_2$, and NaOH (Britton *et al.*, 2005). Struvite precipitates quicker at pH greater than 8.5; however, calcium hydroxide precipitates inhibit struvite formation (Mavinic et al., 2007). Addition of excess magnesium and seeding of struvite crystals can be used to provide the same results at lower pH's (Hao *et al.*, 2013). In pilot scale testing, 80% P removal was found at pH's greater than 8.4 and 50% P removal was found at pH near 7.7 (Britton *et al.*, 2005). Higher pH values are recommended to maintan greater than 80% removal; however, some pilot studies have resulted in greater than 95% P removal at pH=7.6 (Adnan *et al.*, 2003). Typically sodium hydroxide (NaOH) is used to raise the pH and magnesium hydroxide ($Mg(OH)_2$) or magnesium chloride ($MgCl_2$) is used as the magnesium source. Magnesium is typically dosed at a molar ratio of 1.1-1.5:1 Mg:P (Bhuiyan et al., 2008) (Mavinic et al., 2007). The advantage of precipitation of P as struvite is that it can be used beneficially as a slow-release fertilizer (Forrest et al., 2008; Munch and Barr, 2001).

Solids dewatering supernatant is the focus for most research and processes utilizing struvite precipitation (Bhuyian *et al.*, 2008). This stream has a low volume and high concentration of PO_4^{-3} and NH_4^+ (Munch and Barr, 2001). However, since the molar concentration of NH_4^+ is much greater than PO_4-P (10-25:1 N:P), most of the NH_4^+ remains in the liquid phase unless a P source such as phosphoric acid is added as a supplement (Mavinic et al., 2007). Also, sidestream precipitation could only supplement a nutrient removal process in the mainstream, which is necessary to meet discharge permits. This precipitation reaction could be performed in the AnMBR permeate; however, due to the high volume of water and low nutrient concentrations, the chemical costs for pH adjustment and magnesium addition would not be economically beneficial. Therefore this process is suitable for SDS and the concentrated IX regenerant produced from the PO_4^{-3} and NH_4^+ IX columns. The regenerant pH should be considered when determining media for IX as excess amounts of pH adjustment chemicals could be necessary in certain situations.

No studies have reported the efficiency of struvite precipitation in AnMBR permeat; however, previous research has been completed using struvite precipitation in regeneration eluate from aerobically treated municipal wastewater. The first process developed for IX and struvite recovery is called REM-NUT (Petruzzelli *et al.*, 2004). This process includes two IX columns treating secondary clarifier effluent, one with LayneRT™ for removal of PO_4^{-3} and one with clinoptilolite for NH_4^+ removal. Theoretically with this process, about 10% of the zeolite regenerant is added to the LayneRT™ regenerant along with $MgCl_2$ and NaOH to precipitate struvite; however, no precipitation experiments were reported (Petruzzelli *et al.*, 2004). Using regenerant from anion exchange columns, Sengupta and Pandit (2011) precipitated struvite by adding $MgSO_4$ and NH_4Cl. Greater than 90% of the PO_4^{-3} was recovered as a high-value fertilizer; resins regenerated in this study included the following: LayneRT™, DOW-HFO, and DOW-FeCu (Sengupta and Pandit, 2011). Another study using DOW-Cu IX treating RO concentrate from municipal wastewater treatment, found almost 100% P precipitation at a pH of 9 (Kumar *et al.*, 2007). In this test, NH_4^+ and Mg^{2+} salts were added in a molar ratio of 1.5:1:1 Mg:P:N. One study combined the regenerant from clinoptilolite with LayneRT™ or DOW-HFO-Cu; however, the cation column treated septic tank effluent and the anion columns treated synthetic wastewater (Sengupta, 2013). Greater than 85% of N and P were recovered in the precipitate with no Cu or Fe (Sengupta, 2013). The precipitates from Sengupta (2013) contained 16.4% P and 2.4% N; however, pure struvite contains 14.9% P and 6.6% N.

Struvite is a slow-release fertilizer and has a low solubility at neutral pH values which means that it does not provide excess N and P to plant roots (Shu *et al.*, 2006). Struvite has a high value as an agricultural fertilizer, estimated at $0.1-0.15/lb P (Munch and Barr, 2001; Uysal *et al.*, 2010). One kg of struvite per day as a PO_4-P fertilizer is enough for 2.6 ha of agricultural land (Shu *et al.*, 2006). Dry matter yield and P uptake were shown to be similar between plants fertilized with synthetic struvite, recovered struvite, recovered calcium phosphates, and commercial grade calcium phosphates (Johnston and Richards, 2004). The value of struvite may be dependent upon soil type as the Mg:Ca ratio is important in determining oxygen availability and drainage (Muster *et al.*, 2013).

1.9 Ammonia Distillation and Absorption Review

A process developed in 1998 for NH_3 removal and recovery is the use of vacuum distillation with absorption of the NH_3 gas in acid (USEPA, 1998). Traditionally, NH_3 removal by transfer to the gas phase is accomplished through air or steam stripping; however, this method can require air to liquid ratios of 900:1 (Orentlicher *et al.*, 2007). Vacuum distillation of NH_3 relies on a tank under negative pressure in which high concentration NH_3 wastewater at an elevated pH and temperature (90-110 °F) is sprayed into the tank (Orentlicher *et al.*, 2007). Optimum pH for NH_3 transfer is 10.8-11.5; at this pH essentially no NH_3-N is in the aqueous NH_4^+ form (USEPA, 2000a). Vacuum distillation requires less space, lower temperatures, and about 6 times less energy than traditional NH_3 stripping (Orentlicher *et al.*, 2007; Orentlicher, 2012). Streams typically treated with this process such as anaerobic digester supernatant in municipal wastewater and livestock waste have NH_3-N concentrations of 500 mg/l or greater; traditional NH_3 stripping is only economical at concentrations less than 100 mg/l (Orentlicher *et al.*, 2007; USEPA, 2000a). When using vacuum distillation to remove 500-1000 mg/l NH_3-N streams, effluent NH_3-N concentrations are less than 100 mg/l (CASTion, 2008).

Ammonia gas from the vacuum distillation step is absorbed in an acid as a recoverable product. Typically H_2SO_4 is used to absorb the NH_3 gas in a solution containing 40% $(NH_4)_2SO_4$ (USEPA, 1993). However, water can be used as the absorption solution to yield at 1-30% NH_4^+ solution (USEPA, 1980). About 90% recovery is expected with absorption towers (USEPA, 1980). The $(NH_4)_2SO_4$ or aqueous NH_4^+ solution can be sold as an agricultural fertilizer. $(NH_4)_2SO_4$ has value as a commercial grade fertilizer; however, $(NH_4)_2SO_4$ has an acidifying effect on the soil that farmers do not desire (Evans, 2009). The 2011 prices paid for NH_4NO_3, $(NH_4)_2SO_4$, and aqueous NH_4^+ are 479, 423, and 249 \$/ton, respectively (Orentlicher, 2012). Other options for acid used to recover NH_3 include: HNO_3, HCl, and H_2CO_3 (requires passing CO_2 through water to reduce pH). However, NH_4NO_3 is an explosive hazard and the value of NH_4Cl and NH_4HCO_3 is low.

2 Materials and Methods

2.1 Research Questions and Hypotheses

Batch and column ion exchange testing was conducted for removal and concentration of PO_4^{-3} and NH_4^+. Batch tests were conducted to determine parameters that would consume too much time with columns and column testing was conducted to simulate real operating conditions. The present study used wastewater from South Shore Water Reclamation Facility (SSWRF) in Milwaukee, WI as column influent; the wastewater was dosed with N and P to obtain wastewater similar to AnMBR permeate. Regenerant with concentrated N and P was utilized for precipitation of struvite. Each unit process was evaluated individually and then a systems evaluation was conducted to determine the effect of a single process on downstream processes.

2.1.3 Phosphate Ion Exchange Research Questions

A few PO_4-P -selective media have been developed and tested in the literature, including: Dow-Cu, Dow-HFO, Dow-HFO-Cu, activated alumina and LayneRT™ (Hano *et al.*, 1997; Sengupta, 2013; Zhao and Sengupta, 1998). Although these materials have been used in various studies, Dow-HFO-Cu has not been tested in real wastewater. Neutral pH regenerant has not been tested in the literature; either acidic or basic solutions are used (Kumar *et al.*, 2007; Sengupta and Pandit, 2011; Zhao and Sengupta, 1998). Metals concentration and pH of regeneration eluate have not been determined in the literature. Batch testing was conducted to determine relative exchange capacity of the various anion media. Column testing was conducted in order to determine realistic operating conditions for PO_4-P IX. The outcomes to be tested and hypotheses for each test are listed below:

1. What is the percent removal of P in synthetic solution batch tests utilizing various IX media?
    a. Hypothesis: Removal of P will be greatest for LayneRT™ or Dow-HFO-Cu
2. What is the removal capacity (g P/$L_{IX\ bed}$) and effluent PO_4-P concentration for the various IX media in SSWRF secondary effluent dosed with P?
    a. Hypothesis: Resins that removed the most P in batch tests will perform similarly in column testing, but may be slightly different due to a change in water-solid interaction.
    b. Hypothesis: Effluent from PO_4-P IX will contain PO_4-P<0.1 mg/l.
3. What are the pH, metals concentration, and PO_4-P concentration of regenerant from each media?
    a. Hypothesis: Regenerant pH will change across the IX bed as a result of OH^- sorption onto the media and PO_4-P release and H^+ uptake to form $H_2PO_4^{-2}$ or HPO_4^-.
    b. Hypothesis: Significant concentrations of metals such as Fe^{2+} and Cu^{2+} in the regeneration eluate are expected as a result of release from the media.
4. Can the media be regenerated with a neutral pH solution to reduce chemical consumption during struvite precipitation or solution disposal?
    a. Neutral pH regenerant can be used for DOW-HFO and DOW-HFO-Cu as HFO particles are formed at a neutral pH.

2.1.2 Ammonium Ion Exchange Research Questions

Zeolite is shown to selectively removed NH_4^+ in the presence of other cations (USEPA, 1993). Zeolite has been studied for NH_4^+ removal from secondary wastewater, solids dewatering supernatant, source separated urine, and other solutions (Beler-Baykal *et al.*, 2011; Cooney and Booker, 1999; Jorgensen and Weatherley, 2003; Wirthensohn *et al.*, 2009). Optimum NaCl and NaOH regenerant concentrations have also been studied (Guo *et al.*, 2013; Koon and Kauffman, 1975). Research shows that zeolite attrition occurs with high pH regeneration (Koon and Kauffman, 1975). In order to directly compare a variety of NaCl and high pH solutions for regeneration, long-term batch studies to determine the various regenerants' effect on NH_4-N removal capacity were conducted. Column testing of zeolite was conducted to determine the removal of NH_4-N in SSWRF wastewater and the characteristics of zeolite regeneration eluate. The following questions were investigated:

1. What is the optimal NaCl concentration and pH for NH_4^+ desorption and subsequent IX?
    a. Hypothesis: Regeneration at high pH with x% NaCl will be more effective in desorption than regeneration at neutral pH with x% NaCl.
    b. Hypothesis: There will be a pH of regenerant at which N removal capacity in subsequent IX cycles will decrease in comparison to neutral pH regeneration.
2. How much NH_4-N can be removed from SSWRF secondary effluent dosed with N using zeolite and what is the effluent quality?

   a. Hypothesis: Around 130 BV of secondary wastewater can be treated with zeolite before breakthrough; however, the exact amount will be depedent upon K^+, Ca^{2+}, and Mg^{2+} concentration.
   b. Hypothesis: Effluent from NH_4-N IX will contain NH_4-N<1 mg/l.

3. What are the characteristics of zeolite regeneration eluate?
   a. Hypothesis: There will be significant concentrations of NH_4-N, K^+, Ca^{2+}, Mg^{2+}, and Na^+. The pH of the solution will be similar to the influent since OH^- ions are not exchanging with the media.

2.1.3 Struvite Precipitation Research Questions

Struvite precipitation has been well-defined for P removal in solids dewatering supernatant and source-separated urine (Bhuiyan *et al.*, 2008; Forrest *et al.*, 2008; Maurer *et al.*, 2006). In addition struvite precipitation from the combination of anion and zeolite regenerant has been proposed (Petruzzelli *et al.*, 2004; Sengupta, 2013). However, the work by Sengupta (2013) is currently the only published data combining regenerants from both IX media to precipitate struvite. Synthetic solutions are treated by anion media and septic effluent is treated by zeolite media in Sengupta (2013); therefore, exchanged ions may differ and subsequently regenerant characteristics may differ in comparison to a system treating secondary effluent dosed with N and P. Additionally, large volumes of regenerant were required, greater than 20 BV, likely diluting the N and P. Greater than 85% removal of N and P were obtained from the combination of LayneRT™ or Dow-HFO-Cu regenerant with zeolite regenerant; solids were claimed to be high purity struvite, but there is only 33% as much N in the solids as there would be in pure struvite

(Sengupta, 2013). The present work treated the same wastewater with the anion and cation column and utilized a small volume of neutral pH solution to regenerate the iron and copper loaded resin. Struvite precipitation of the combined regenerants was tested in batch mode and the following questions were answered:

1. What percentage removal of N and P can be accomplished with struvite precipitation of anion and zeolite regeneration eluates?
    a. Hypothesis: Provided there are enough cations such as Mg^{2+} in solution, greater than 85% of P will be removed. Removal of N will be dependent upon the amount of P removed as $MgNH_4PO_4$ versus other solids.
2. What impurities are found in the recovered solids?
    a. Hypothesis: Given that Ca^{2+}, K^+, Fe^{2+}, and Cu^{2+} potentially leach or desorb from the zeolite or anionic media, a number of non-$MgNH_4PO_4$ solids will form. Given these cations, there is the potential to form $Ca(OH)_2$, $Ca_3(PO_4)_2$, hydroxyapatite, $MgKPO_4$, $Fe(OH)_2$, vivianite, and $Cu(OH)_2$.

2.2 Selection and Preparation of Ion Exchange Materials

Clinoptilolite was selected as the media for NH_4^+ exchange due to its preference for NH_4^+ in the presence of other cations (USEPA, 1993). Clinoptilolite, (St. Cloud Zeolite, Tucson, AZ, USA) in the sodium aluminosilicate form had a cation exchange capacity of 1.85 meq/g. Preparation of clinoptilolite to saturate the surface with Na^+ ions was accomplished through the following steps: rinse 25 g of material 3x to remove fine particles, soak in 1% NaCl on shaker table at 150 rpm for 2 days, remove NaCl solution and rinse 2x with deionized (DI) water, dry material at 103 °C for 24 hours. Preparation of clinoptilolite is similar to methods reported by Guo *et al.* (2013) and Jorgensen and Weatherley (2003).

In order to test a non-specific exchange resin, commercially available P selective resin, and laboratory prepared P selective resins, the following media were purchased: Dowex WBA-2 (Dow Chemical Co., Midland, MI, USA), Dowex M4195 (Dow Chemical Co., Midland, MI, USA) and LayneRT™ (Layne Company, Mission Woods, KS). Dow WBA-2 is a non-specific weak-base anion exchanger with a 1.7 eq/L exchange capacity and an average particle size of 0.55 mm. The shipping density of this resin is 640 g/L. This resin was utilized to examine the competitive uptake between PO_4-P and other anions in a general resin versus a PO_4-P selective resin. Regeneration of Dow-WBA-2 is typically performed with 2-4 BV of 2-5% NaOH (DOW, 2013). Dowex M4195 is an anion exchange resin with tertiary amine groups with a particle size of 0.3-0.841 mm and a bulk density of about 670 g/L. This resin is used as a base resin to develop chelating resins; loading of metals may include iron, copper, aluminum, or some combination thereof. Finally, LayneRT™ is an iron-loaded resin selective towards PO_4-P and is regenerated with an equal mixture of NaCl and NaOH. Density of LayneRT™ is 790-840 g/L with a particle size of 0.3-1.2 mm (Sengupta, 2013).

2.3 Ammonium Ion Exchange Batch Testing

Batch testing of NH_4^+ removal using clinoptilolite was conducted with NH_4^+ only solution and a mixed cation solution, both containing about 40 mg/l NH_4-N. Bottles used for batch testing were completely filled with 128 mL of solution, leaving no headspace for ammonia volatilization. The concentration of zeolite was 10 g/l or 1.28 g in the 128 mL bottles and they were placed on a shaker table at 150 rpm. NH_4-N only solution was made by adding 1.53 g of NH_4Cl to 1000 mL MilliQ (0.22µm pore size) water and then diluting the solution by a factor of 10; the target NH_4-N concentration was 40 mg/l. To determine the required test duration, batch equilibrium was measured by setting up two bottles for each day of analysis. One bottle contained zeolite and the other did not as a control to account for ammonia absorption to the glass. Analysis was conducted after 1, 2, 3, 4 and 6 days. Once the percent change, as defined by Equation 3, was less than 5%, equilibrium was assumed to be reached.

$$\% \, Change = \frac{(Sorption_n - Sorption_{n-1})}{(Sorption_n) * t_{n-1}} * 100 \qquad \text{Equation (3)}$$

Where,

Sorption = mg NH_4-N removed/g zeolite

n = day

t = time difference between samples (days)

The time to equilibrium was utilized to conduct all further zeolite batch tests.

NH_4-N only batch testing was conducted using the chemical solution, rotation speed, equilibrium, and media concentration described previously. After the equilibrium time was reached, solution was analyzed for NH_4-N concentration and then the liquid was decanted while retaining the zeolite. Next, regenerant was added to the bottles for 2 hours; the solution was sampled, removed, and the zeolite was rinsed 2 times to remove excess salts. The batch testing process is depicted in Figure 6.

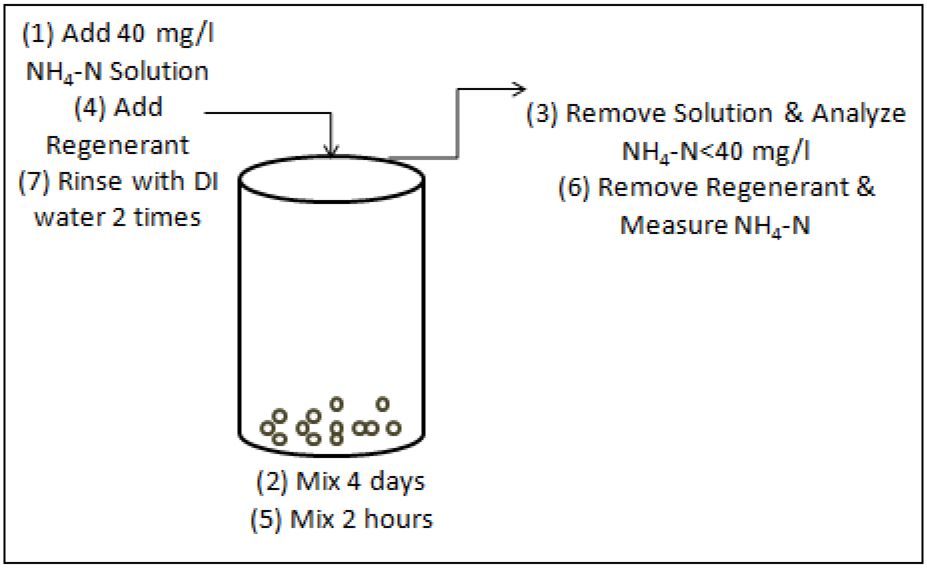

Figure 6: The steps to NH_4-N batch testing

A variety of regenerants based upon a literature review were developed in order to determine the effect of each solution on subsequent IX capacity. Triplicate bottles were prepared for each regenerant condition. Five regenerant solutions were tested for 3 IX cycles, while two more regenerant solutions were tested for 7 IX cycles. Solutions tested for 3 cycles include the following: 2% NaOH, 2% $Ca(OH)_2$, 10% NaCl, 5% NaCl, and 0.5% NaOH. The most effective neutral and high pH regenerants were tested for 7 IX cycles; these regenerants were 8% NaCl and 7.5% NaCl + 0.5% NaOH. Evaluation of the results was based on percent removal of NH_4-N during IX and regeneration NH_4-N concentration.

After NH_4-N only testing, mixed cation IX batch testing was conducted in order to determine competitive uptake of cations. Regenerant solution utilized were revised based on results from NH_4-N only IX testing. The same zeolite dose, solution volume, and exchange time were used in the mixed cation batch tests. Mixed cation solution contained 1.53 g NH_4Cl, 0.38 g KCl, 5.08 g NaCl, 1.38 g $CaCl_2$, and 2.1 g $MgCl_2*6H_2O$. This solution was then diluted by a factor of 10 with target concentrations of 40 mg/l NH_4-N, 20 mg/l K^+, 50 mg/l Ca^{2+}, 25 mg/l Mg^{2+}, and 200 mg/l Na^+; these concentrations were based on typical primary effluent concentrations (Metcalf and Eddy, 2003). Regeneration solutions selected for this test included 8% NaCl, 7.5% NaCl (pH=12), 0.1% NaOH, and 0.1% $Ca(OH)_2$. Testing was carried out for 5 IX cycles and results were analyzed based on the same two parameters discussed in the NH_4-N only tests as well as the separation factor. The separation factor describes the preference of a media for exchange of one ion over another. Knowing preference for exchange of NH_4^+ over other cations will determine which cations should be considered when designing the amount of wastewater an IX column will handle.

2.4 Phosphate Ion Exchange Batch Testing

In addition to the two resins purchased in ready-to-use form, six chelating anionic resins were created using previous literature and novel methods. The base resin for all six chelating resins was Dowex M4195 (DOW Chemical Co., Midland, MI). A list of resins is given in Table 2.

Table 2: Chelating phosphate selective resins

Name	Dow-Cu	Dow-HFO	Dow-FeCu	Dow-HFO-Cu	Dow-NAB-Cu	Dow-Al
Metal Solution Utilized	$CuCl_2$	$FeCl_3$	$CuCl_2$ & $FeCl_3$	$CuCl_2$ & $FeCl_3$	$CuCl_2$	$Al_2(SO_4)_3$

The first resin undergoes acid and base treatment followed by copper loading; this resin is denoted DOW-Cu. The protocol for loading was derived from previous work where the resin was prepared in column mode (Zhao and Sengupta, 1996). In a 1 L bottle, 10 g of Dowex M4195 was mixed with 100 mL of 1 N HCl and placed on a shaker table for 2 hours. The acid was removed, the resin rinsed twice with DI water and then 1 L of 1 N NaOH solution was added to the bottle of resin. This mixture was also placed on a shaker table for 2 hours, then it was removed, and the resin was rinsed twice with DI water. Finally, 1 L of 500 mg/l Cu^{2+} solution (1.34 g $CuCl_2$*$2H_2O$ in 1 L DI water) was added to the bottle. After 24 hours, the Cu^{2+} solution was decanted and the resin was rinsed twice with DI water and allowed to air dry at 35 °C for 48 hours. Another resin, loaded with ferric chloride (DOW-HFO) was prepared using methods previously discussed by Sengupta and Pandit (2011) with the exception of drying the resin at 35 °C instead of 45 °C. A resin combining the previous two methods was produced by first preparing Dowex M4195 with the ferric chloride method and then the cupric chloride method; this resin was denoted as DOW-FeCu. The iron and copper loaded resin method of preparation was revised to be similar to that described by Sengupta (2013); this resin was called DOW-HFO-Cu. Ten grams of Dowex M4195 was added to 40 g $FeCl_3$*$6H_2O$ in 3 L of MilliQ water. The pH was adjusted to 8 over a period of 4 hours using NaOH tablets. The resin was then stirred for 24 hours followed by decanting of the iron solution and rinsing of the resin with DI water to remove all iron precipitates. Solution containing 1.33% $CuCl_2$*$5H_2O$ was added to the bottle of resin and allowed to stir for 24 hours. The copper solution was decanted and the resin was rinsed with DI water and allowed to dry at 35 °C for 24 hours.

Two of the six metal-loaded resins were prepared by novel methods. The first was copper loaded Dowex M4195 (Dow-NAB-Cu) without acid and base pretreatment. The purpose was to determine if the extreme pH solutions used in preparation of DOW-Cu were necessary. This was accomplished by soaking 10 g of Dowex M4195 in 1 L of 500 mg/l Cu solution formed from 1.34 g $CuCl_2*2H_2O$ in 1 L MilliQ water. The resin and solution mixture was placed on a shaker table for 24 hours, then the solution was discarded, the resin was rinsed twice with DI water, and allowed to dry at 35 °C for 48 hours. The next resin was Dowex M4195 loaded with aluminum sulfate (DOW-Al) by a method derived from a patent for loading an anion resin with iron (Sengupta and Cumbal, 2007). Ten grams of Dowex M4195 was added to 1 L of 500 mg/l $KMnO_4$ solution. This mixture was allowed to stir for 30 minutes and then the solution was discarded and the resin was rinsed twice with DI water. Next 1 L of 2% $Al_2(SO_4)_3*7H_2O$ (alum) was added to the bottle of resin and allowed to stir for 24 hours. After the given time period, the mixture was passed through a 45 μm sieve to remove all aluminum precipitates and then the resin was allowed to dry for 48 hours at 35 °C.

PO_4-P -only batch testing was conducted using the following media: Dowex WBA-2, Dowex M4195, LayneRT™ and weakly acidic activated alumina (AA) (Sigma Aldrich, Milwaukee, WI, USA). PO_4-P solution was prepared by adding 0.45 g of $NaH_2PO_4*H_2O$ to 1 L of MilliQ water. This solution was then diluted by a factor of 10 to obtain a solution with a PO_4-P concentration around 3 mg/l. Media were dosed into 128 mL of solution at a concentration of 10 g/l; bottles were placed on a shaker table at 150 rpm for 7 days. Triplicate bottles were set up for each media and triplicate bottles without media were run to account for PO_4-P absorption to the glass. After 7 days, the solution was analyzed for PO_4-P concentration and the media were regenerated with 6% NaCl at pH=10 for 2 hours. Percent PO_4-P removal during IX and regenerant PO_4-P concentration were determined.

After PO_4-P only testing, the same media were tested using a mixed anion solution. Solution volume, rotation speed and media dosing remained the same, while the IX time was reduced to 4 days to match zeolite batch testing. The targeted concentrations in mixed anion solution were 3.9 mg/l PO_4-P, 150 mg/l HCO_3^-, 5 mg/l SO_4-S, 5 mg/l S^{2-}, and 50 mg/l Cl^-. Concentrations were selected based on a literature review of typical wastewater influent and AnMBR permeate characteristics (Gimenez *et al.*, 2011; Metcalf and Eddy, 2003; Yoo *et al.*, 2012). The following mass of chemicals was added to the 10 times concentrated solution: 0.22 g K_2HPO_4, 2.07 g $NaHCO_3$, 0.22 g Na_2SO_4, 0.12 g $NaSH*nH_2O$ (74% NaSH), and 0.82 g NaCl. Final concentration of each anion was measured to determine each media's affinity towards specific anions. Regenerants used in the mixed anion tests were dependent upon the material. A solution of 5% NaCl (pH=10) was used for Dowex WBA2 and Dowex M4195 while 2% NaCl+2% NaOH was used for LayneRT™ based on a literature review (Blaney *et al.*, 2007). Regenerant for AA was 2% NaOH which was based on previous work in the literature (Ames, Jr. and Dean, 1970). Regeneration was conducted for 2 hours with 2 DI rinse cycles following the regenerant analysis. Data analysis included percent removal during IX for anions and the concentration of PO_4-P in the regenerant.

The final batch test was a high-concentration (spiked) PO_4-P test to determine the difference in exchange capacity of various resins. Media utilized for this test included the following: AA-neutral, AA-basic, Dow-Cu, Dow-NAB-Cu, DOW-HFO, LayneRT™, DOW-FeCu, and DOW-Al. Media was dosed at 10 g/l in 128 mL of 100 mg/l PO_4-P solution. PO_4-P solution was created by adding 1.124 g K_2HPO_4 to 2 L of MilliQ water; the pH of this solution was about 8.1. The bottles were placed on a shaker table at 150 rpm for 4 days. All bottles were run in triplicate and controls were run to account for PO_4-P absorption to the glass. PO_4-P concentration and pH at the end of the test were measured. Percent removal of PO_4-P was calculated using the results from the controls.

After completion of IX with spiked PO_4-P batch tests, regeneration was conducted in order to determine the potential for recovery. Solutions contained various concentrations of NaCl and NaOH based either literature reported solutions or a reduction in chemicals in comparison to the literature. Solutions used in the literature can be found in Table 1 and regenerants used for the spiked P test are displayed in Table 3.

Table 3: List of anion media and regenerants used in PO_4-P IX batch testing

Media	AA neutral	AA basic	LayneRT™	Dow-Cu	Dow-NAB-Cu	Dow-HFO	Dow-FeCu
Regenerant	5% NaCl pH=7.5	5% NaCl pH=9.5	2% NaCl + 2% NaOH	5% NaCl pH=4.3	5% NaCl pH=4.3	5% NaCl pH=8	5% NaCl pH=8

Regeneration was performed with 128 mL of solution and the bottles were placed on a shaker table at 150 rpm for 4 hours. Final pH and PO_4-P concentration were measured; percent desorption of PO_4-P was calculated as the comparable result. The PO_4-P batch IX and regeneration steps are depicted in Figure 7.

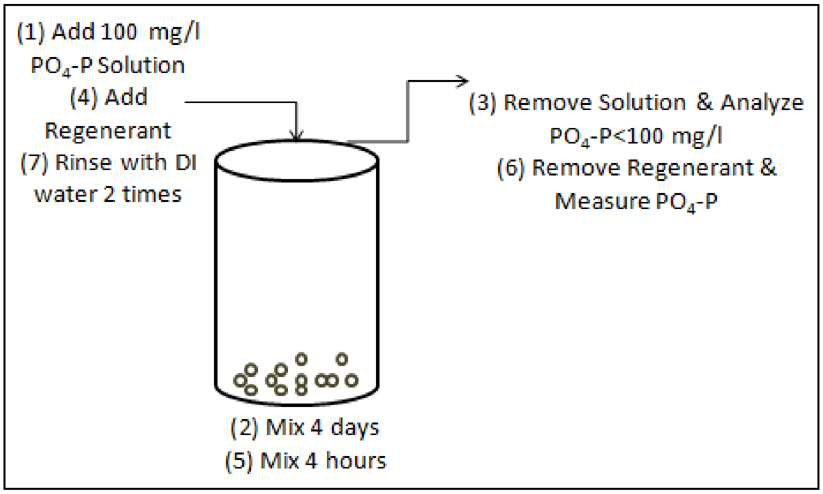

Figure 7: The steps to PO_4-P batch testing

2.5 Column Testing

The 3 media with greatest PO_4^{-3} exchange in batch studies were tested in column mode, LayneRT™, Dow-Cu, and Dow-FeCu. Testing the materials in columns was important as full-scale systems would be operated in columns and the solution-solid contact is different in columns compared to batch tests and as a result, the exchange kinetics are different. Anion column testing was conducted using secondary effluent from SSWRF. The secondary effluent was dosed with $(NH_4)_2HPO_4$ and NH_4Cl to approximately 4-6.5 mg/l PO_4-P and 30-35 mg/l NH_4-N to simulate anaerobic membrane permeate from municipal wastewater treatment. The sample was filtered using a 1.5 µm filter. Anion concentrations measured in the sample include PO_4-P, Cl^-, SO_4-S, S^{2-}, NO_3-N, and bicarbonate. The column, which was 2.5 cm in diameter, was filled with PO_4-P exchange media to a 7.5 cm height. Media volume was approximately 35-37 mL and exact volume was measured and used in calculations. Samples were stored at 3 °C for up to 2 months. Each day the sample was prepared by filtration, equilibration to 22 ºC and then added to the influent tank. Flow rate through the system was maintained at 3 Lpd or 3.4 BV/hr. This flow rate provided an empty bed contact time (EBCT) of 17.6 min. Contact time was greater than previous work with EBCTs of 6-8 min in order to ensure that multiple samples would be collected during breakthrough with 2 hr sampling intervals (Kumar *et al.*, 2007; Petruzzelli *et al.*, 2003. Influent and effluent pH were recorded for each column test. A water head of about 3 inches was maintained above the IX media in order to eliminate short circuiting of the system and disruption of the bed due to influent droplets. Effluent was directed to a valve that was opened every 2 hours for a period of 20 mins. When this valve was open, sample was sent to a fraction collector (CF-1, Spectrum Chromatography, Houston, TX) and when the valve was closed, the effluent was discarded. Twelve samples were measured each day for PO_4-P and 3 – 5 samples from the test were measured for metals. The IX column system is displayed in Figure 8.

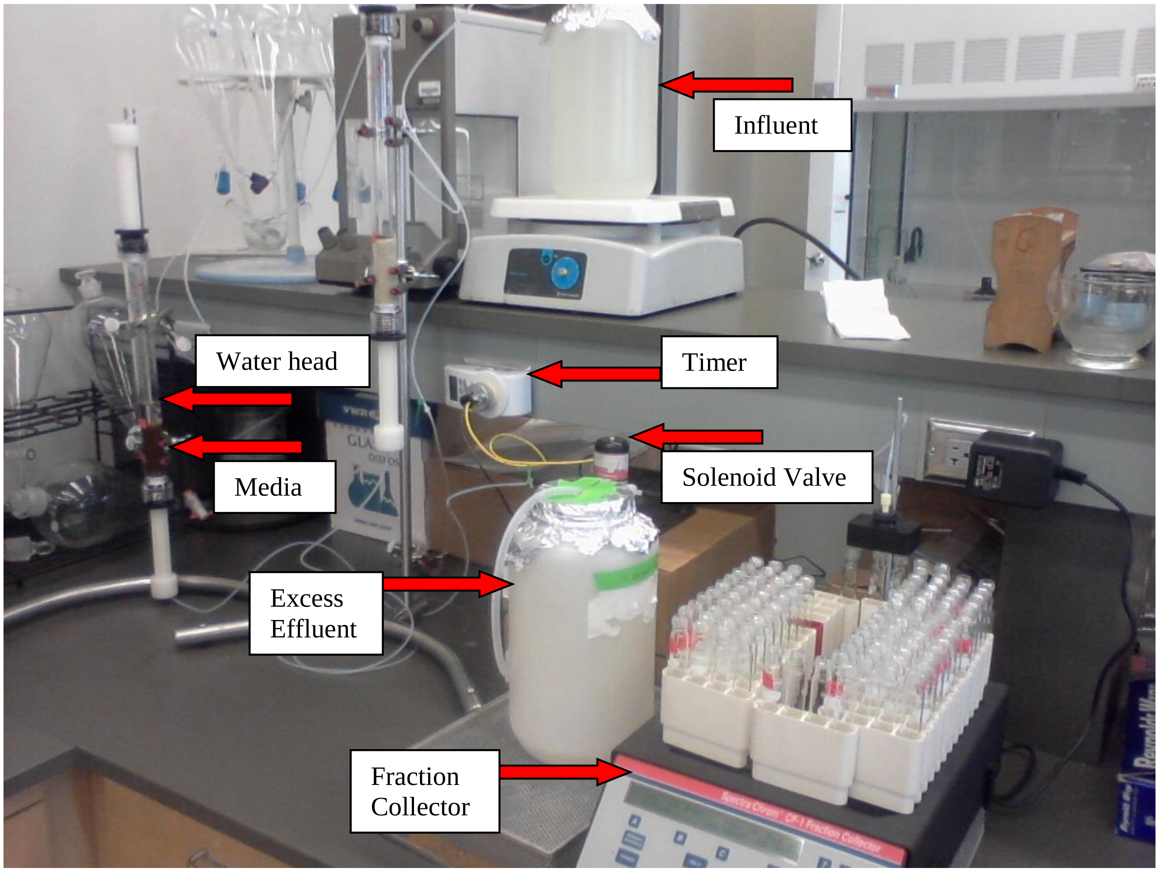

Figure 8: Phosphate IX column testing apparatus

PO_4-P discharge was calculated by fitting a curve to multiple sections of the effluent PO_4-P curve using Microsoft Excel and integrating the curve to obtain the area (mass of PO_4-P leaving the system). Exchanged P was calculated as influent mass minus effluent mass.

Clinoptilolite was used as the media in cation exchange column testing. Bed volume of the mineral was 37 mL; the column diameter and height were 2.5 and 7.5 cm, respectively. Effluent from the LayneRT™ column test was used as influent to the clinoptilolite column. The sample was allowed to mix on a stir plate until reaching room temperature, 20 °C; sample was stored at 4 ºC for up to 45 days. NH_4-N was measured in the sample prior to pumping the wastewater into the IX column. Metals including, Na^+,

Mg^{2+}, Ca^{2+}, K^{+}, and 16 others were measured in the sample; all cations measured are listed in the analytical section. A water head of about 3 inches was maintained in the column for the same reasons as during anion exchange. Using a peristaltic pump, wastewater sample was pumped through the column at a rate of 3 Lpd or 3.4 BV/hr. Effluent was collected just as with the anion exchange column. The pH of the influent and effluent were recorded. Regression lines for multiple sections of the plot, effluent NH_4-N versus volume treated, were developed using Microsoft Excel and these curves were integrated to determine the area (mass of NH_4-N leaving the system). Exchanged NH_4-N was calculated as described for P in the previous section.

2.6 Column Regeneration

Regeneration of the anion columns was conducted following exhaustion of the media's exchange capacity. Different solutions were mixed for each of the resins; LayneRT™, DOW-Cu, and DOW-FeCu were regenerated with 2% NaCl + 2% NaOH, 6% NaCl (pH=4.3), and 6% NaCl (pH=8), respectively. Solution was passed through the IX bed at a rate of 125 mL/hr or 3.4 BV/hr; as during IX, a water head of around 3 inches was maintained above the media. Five mL of sample was collected continuously until about 50 mL had passed and then sample was collected approximately after every 30 mL of solution passed; PO_4-P measurements were used to develop a curve of PO_4-P concentration versus BV passed. Regenerant sample was diluted 1/1000, 1/100 or 1/10 depending on the time of collection to enable sample quantification within a measureable range. Once the regenerant concentration was below 10 mg/l PO_4-P, the test was ended. Total desorption of PO_4-P was calculated by fitting regression lines to the regenerant

PO_4-P concentration curve. Regenerant was preserved by collecting effluent in a bottle during the first 7 BV for LayneRT™ and the first 4 BV for other resins since desorption was negligible after 4 BV. Solution was preserved at 4 °C for struvite precipitation tests; the pH of this solution was recorded and PO_4-P concentration was measured. Concentration of metals in the regenerant was measured as described in the analytical section; ions of greatest interest were Al^{3+}, Fe^{2+}, and Cu^{2+}. After regeneration, the bed was rinsed with 150 mL of MilliQ water and then air was pumped through the column to remove all liquid to prevent metal leaching while the bed was not in operation.

Clinoptilolite was regenerated using 6% NaCl at a pH of 11. Flow rates and operating conditions were the same as with the anion regeneration. Four mL of regenerant sample was collected in a bottle containing 1 mL of 1% H_2SO_4 to prevent ammonia volatilization; collection occurred in intervals of approximately every 10-30 mL. The sample was diluted 1/5000, 1/500 or 1/100 based upon the time of collection to enable sample quantification within the detection range. Regression curves were developed for effluent NH_4-N versus BV passed in order to determine total desorption and NH_4-N concentration of the first 8 BV. Regenerant from the first 8 BV was preserved by collection in a bottle and storage at 4 °C; the pH of this solution was recorded and NH_4-N was measured. Preservation of the regeneration eluate was conducted for later use in struvite precipitation tests. Metals concentration in this regenerant was measured; specifically Mg^{2+}, Ca^{2+}, K^+, Na^+, Al^{3+}, and Fe^{2+} were of interest. The clinoptilolite bed was rinsed with 150 mL of DI water prior to running a second IX cycle.

2.7 Struvite Precipitation

Struvite precipitation was first conducted using laboratory grade chemicals. Struvite containing NH_4^+ (N-struvite) and struvite containing K (K-struvite) were precipitated. Struvite formed with K ($MgKPO_4$) was precipitated as an alternative to $MgNH_4PO_4$ to obtain data in the case of targeting K recovery instead of N. The goal was to determine pH of minimum solubility and the requirements for ion molar ratios for K-struvite; N-struvite precipitation was conducted for direct comparison to K-struvite. Molar ratios of Mg:N:P and Mg:K:P were targeted at 1:1:1. For K-struvite precipitation, 90 mL of solution containing 2.32 g of $MgCl_2$*6H_2O and 0.61 g KCl per L was added to 10 mL of solution containing 1.14 g Na_2PO_4*H_2O per L. Once the solutions were mixed, pH was adjusted using 0.1 N NaOH and 0.1 N HCl. Seven Erlenmeyer flasks with a range of pH from 8.1 to 13.3 were prepared with the mixture of solutions. Flasks were placed on a shaker table at 150 rpm for 10 minutes and then the solids were allowed to settle for 30 minutes. After the settling period, supernatant was sampled for measurement of PO_4-P, K^+, and Mg^{2+}. Remaining sample was then filtered through a 0.45 μm glass fiber filter. The filter was dried in an oven at 105 °C for 24 hrs and the mass of solids was measured. N-struvite was precipitated with the same method except 0.44 g NH_4Cl per L replaced KCl. NH_4-N and Mg^{2+} solution were added in a volume of 90 mL to the 10 mL PO_4^{-3} solution in order to obtain a 1:1:1 Mg:P:N molar ratio. Range of pH tested, pH adjustment chemicals, reaction time and settling time were the same as with K-struvite. Supernatant was sampled for PO_4-P, NH_4-N, and Mg. The solids were again filtered, dried, and weighed.

Once pure solution tests had been performed, regenerants from column testing were used for precipitation of struvite. Zeolite regenerant was used as the NH_4-N source and four anion exchange regenerants were tested as PO_4-P sources for comparison. LayneRT™, DOW-Cu column run 1 (DOW-Cu 1), DOW-Cu column run 2 (DOW-Cu 2), and Dow-FeCu regenerants were used (as described in section 1.4 Nutrient Recovery Scheme). PO_4-P was measured in the anion regenerants and NH_4-N was measured in the zeolite regenerant. Triplicate precipitation tests were run for each anion regenerant in 125 mL Erlenmeyer flasks. Anion regenerant was added in a volume of 40 mL for LayneRT™ precipitation flasks and 30 mL was added to DOW-Cu and Dow-FeCu precipitation flasks. A Mg solution containing 12.5 g $MgCl_2$*$6H_2O$ per L was mixed and 11 mL was added to LayneRT™ precipitation while 2.5 mL was added to the two DOW-Cu precipitation tests; volume of Mg solution is based upon a 1:1 Mg:P molar ratio. Zeolite regenerant was added in a volume of 16 and 3.3 mL to LayneRT™ and DOW-Cu precipitation flasks, respectively, in order to obtain a 1:1 P:N molar ratio. For Dow-FeCu precipitation, 1000 mg/l Mg^{2+} solution and zeolite regenerant were added in volumes of 12.5 and 20 mL, respectively. Once all three solutions were mixed, the pH was adjusted to 10 using 0.1 N NaOH or 1 N HCl. There was a reaction period of 10 minutes at 150 rpm and a settling period of 30 minutes. Supernatant was collected for PO_4-P, NH_4-N and metals analysis. Concentrations of Fe^{2+}, Cu^{2+}, Ca^{2+}, K^+, Mg^{2+}, and Al^{3+} were of interest as they could be desorbed from the resins or zeolite and therefore in the precipitates. A diagram of the full batch struvite precipitation test is shown in Figure 9.

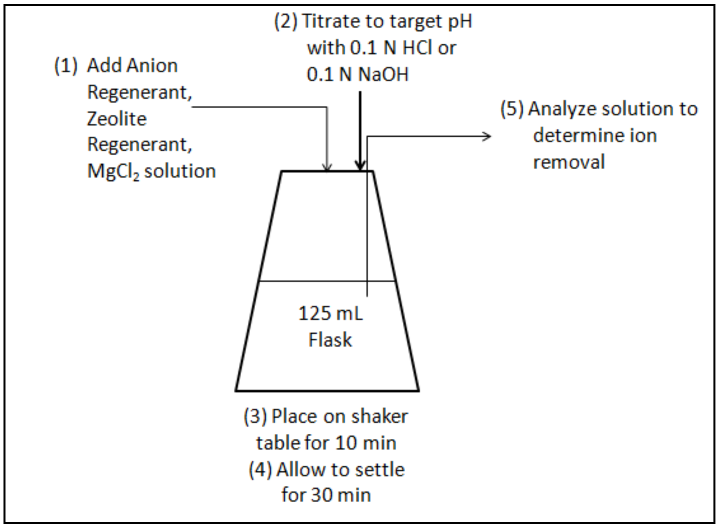

Figure 9: Batch struvite precipitation steps

Mass of solids was measured by filtering the sample through a 0.45 µm glass fiber filter and drying the solids at 105 °C for 24 hrs. Struvite solids were analyzed by nitric acid digestion. Solids dried on glass fiber filters were placed in 100 mL of 0.5% nitric acid for 2 days. Sample was then collected for PO_4-P, NH_4-N, and metals analysis. Results were compared to the mass balance utilizing initial and final solution ion concentration data.

2.8 Analytical Methods

Spectrophotometric methods were used for analysis of NH_4-N, PO_4-P, SO_4^{-2}, Cl^-, and NO_3-N. NH_4-N was measured using the Phenate Method, standard method 4500-NH_3 F, having a range of 0.1-1 mg/l NH_4-N. (APHA *et al.*, 1998). PO_4-P was determined using the ascorbic acid standard method (APHA *et al.*, 1998); this method has a range of 0.006 to 0.8 mg PO_4-P/l. TP was determined using the acid persulfate digestion method followed by the ascorbic acid method for PO_4-P. Mercuric thiocyanate method from

Hach (Loveland, CO) was utilized to determine chloride concentration; the test range was 0 to 25 mg/l Cl^-. Sulfate was determined with a Hach method equivalent to USEPA method 375.4 which can detect sulfate concentrations to a maximum of 70 mg/l. Cadmium reduction method was conducted for nitrate-N analysis with a range of 0 to 0.5 mg NO_3-N/l. Standard solutions of NH_4-N, PO_4-P, SO_4-S, Cl^-, and NO_3-N were created using NH_4Cl, K_2HPO_4, Na_2SO_4, NaCl, and KNO_3, respectively. Absorbance was measured using Thermo Scientific (Waltham, MA) Genysys 20 spectrophotometer. An ICP-MS (7700 Series, Agilent Technologies, Santa Clara, CA, USA) was used to measure Ca, Mg, K, Na, Al, Fe, Cu, Be, Cr, Mn, Co, Ni, Zn, Se, As, Mo, Pb, Hg, Ag, and Cd. Measurement of pH was conducted with a Thermo Scientific Orion 4 STAR pH meter. Biochemical oxygen demand was analyzed using standard method 5210 B; the test was performed in order to conclude whether or not biological fouling was an issue at a given influent BOD concentration (APHA *et al.*, 1998). Polyseed (The Woodlands, TX) microbes were used as the seed for BOD tests. Seed dilutions of 10, 20, 25, and 30 mL were used. Sample was added in a volume of 75 mL with 4 mL of seed. The bottles were allowed to run to 20 days to estimate the ultimate BOD. Hach nitrification inhibitor formula 2533 was used to eliminate nitrification. Alkalinity was determined using standard method 2320 B (APHA *et al.*, 1998).

2.9 Statistical Analysis

Standard deviation (std. dev.) assuming a normal distribution was calculated for mixed cation batch test IX and regeneration. Standard deviation of triplicate tests was used to create error bars for plots; this provides an estimate as to whether sample averages are statistically similar or not. This allowed for determination of significant differences between test conditions, specifically, the statistical difference between regenerants.

In order to determine whether two data sets were statistically similar, a student's t-test was conducted. First an F-test was conducted with a null hypothesis that the variances of two data sets were similar. The function "F.Test" in Excel was used to calculate the F-test p-value. If the p-value was less than 0.05, the null hypothesis was rejected and a type 3 t-test was conducted; if p was greater than 0.05, a type 2 t-test was conducted. A student's t-test was calcualted for mixed cation IX batch tests, spiked PO_4-P IX batch tests, and spiked PO_4-P regeneration batch tests. The test was conducted for comparison of two conditions, for example removal percent of NH_4-N with 8% NaCl versus 7.5% NaCl (pH=12). Statistics were calculated with a two-tailed distribution, type 2 or 3 t-Test using the "TTEST" function in Microsoft Excel. Two test conditions were considered statistically different with 95% confidence if the resulting value was less than 0.05. If the value was greater than 0.05, the two conditions are considered not statistically different.

3 Results and Discussion

3.1 Zeolite NH_4^+ Exchange and Regeneration Batch Testing

Equilibrium for NH_4^+ exchange was tested in order to ensure that batch testing was conducted for a sufficient period to nearly reach equilibrium of solid and liquid phase NH_4^+. If batch testing is ended prior to reaching equilibrium, results may vary and not be accurate. Sorption equilibrium of NH_4-N onto clinoptilolite was reached in 4 days based on less than 5% change in total sorption between days as calculated using Equation 1. Figure 10 displays the sorption of NH_4-N onto clinoptilolite versus time. More than 50% of the sorption occurred within the first day and by Day 4 there was little change in total sorption. Although almost all total sorption was accounted for in the first 3 days, equilibrium was assumed after 4 days in subsequent NH_4-N batch tests.

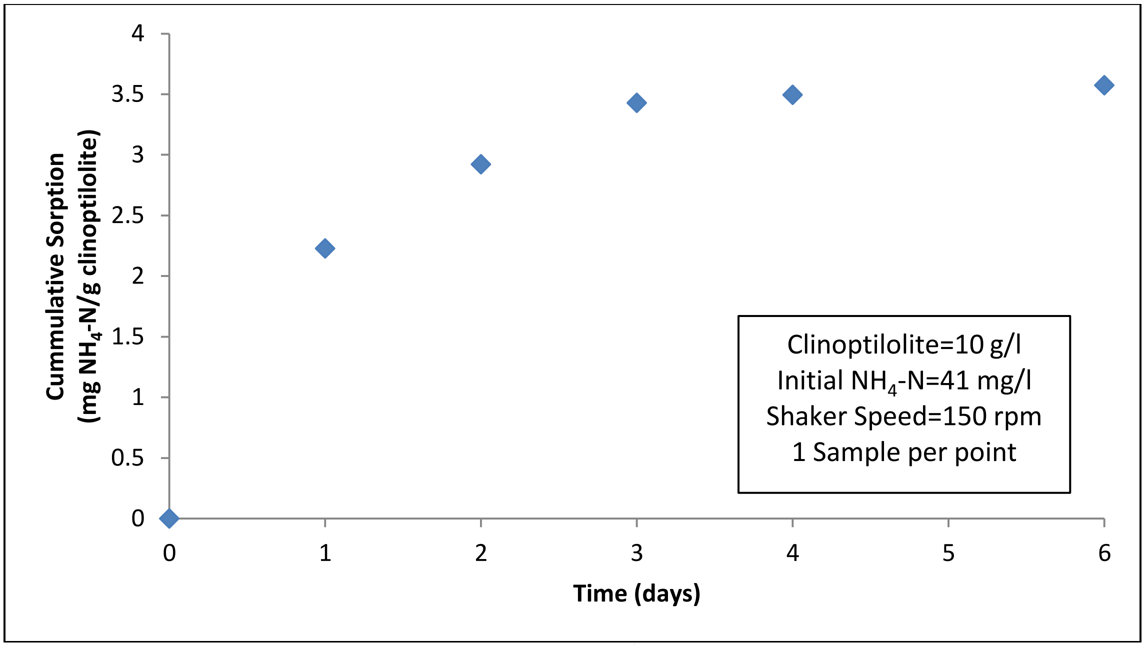

Figure 10: Sorption of NH_4^+ onto clinoptilolite

As sample passes through a column, the aqueous NH_4-N concentration decreases and therefore lower sections of the column are exposed to low NH_4-N concentration. Therefore, a sorption test was conducted to determine the ability of clinoptilolite's to remove NH_4-N in solution at low NH_4-N concentration. This test was conducted with 30 mL of solution, at 150 rpm and a contact time of 2 days. Sorption equilibrium appeared to follow a second-order polynomial curve (see Figure 11). The media achieved NH_4-N concentrations of less than 0.1 mg/l in solution when the initial concentration was less than 4.8 mg/l. Theoretically, the concentration of NH_4-N will continually decrease from the top of an IX column to the point of discharge. Therefore, according to this sorption test, column effluent NH_4-N concentrations could be less than 0.1 mg/l if the bed has sufficient depth.

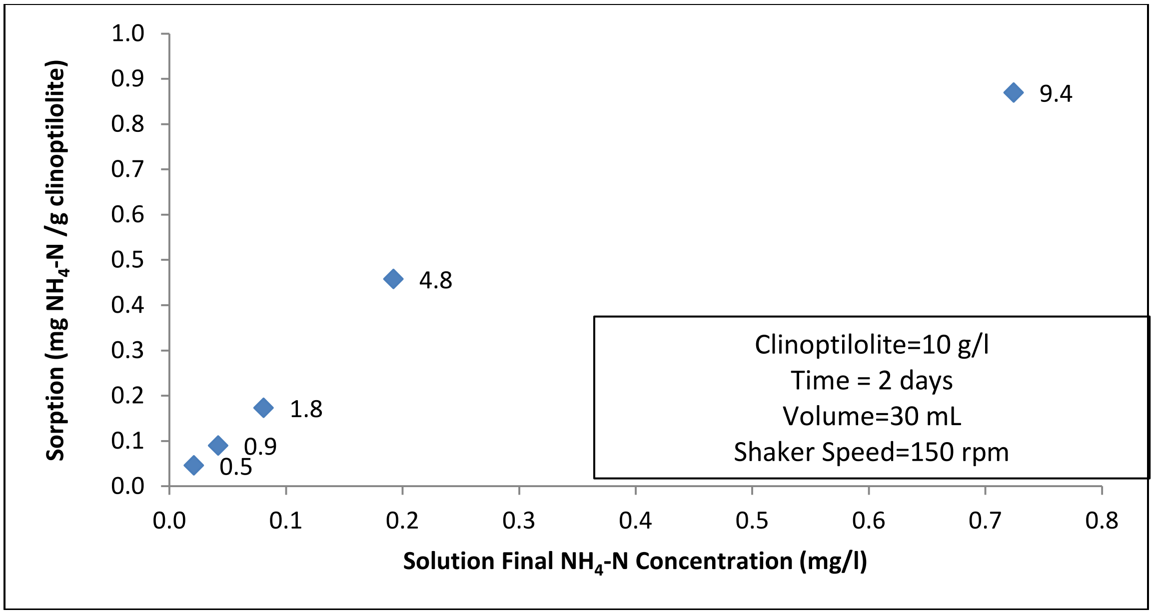

Figure 11: Sorption of NH_4-N onto zeolite vs final NH_4-N concentration; initial NH_4-N labeled next to data point

3.1.1 Zeolite Ion Exchange Batch Testing with Ammonium Chloride

NH_4-N only IX tests were conducted utilizing a variety of regenerants with triplicate bottles for each regenerant. By testing a variety of regenerants, the pH and NaCl for optimal desorption and subsequent IX can be determined. Essentially, the optimal solution requires the least chemicals, provides large N desorption, and maintains IX capacity long-term. A key parameter tested in each IX cycle was percent NH_4-N removal. Percent removal results for multiple cycles could be used to help identify which solutions could be used to regenerate the material with the least exchange capacity loss. Five regenerant solutions were tested for 3 IX cycles after which 2 regenerants were selected to be operated for 7 IX cycles; results are displayed in Figure 8. Removal of NH_4^+ during the first IX cycle was approximately 85-88% for all exchange bottles. Results showed that 8% NaCl was the most effective regenerant in maintaining removal and 10% NaCl, 5% NaCl, and 0.5% NaOH resulted in slightly less removal than 8% NaCl after 3 cycles (Figure 12). Excessive NaOH becomes negatively impacts IX capacity as 0.5% NaOH outperformed 2% NaOH. These results were expected based on the literature; high pH solutions cause attrition of clinoptilolite surface (Koon and Kauffman, 1975). Use of $Ca(OH)_2$ was unsuccessful as much of the calcium remained insoluble. The insoluble calcium was entrapped in the media and therefore disrupted IX processes; previous work has noted $Ca(CO_3)_2$ precipitation within the bed (Sedlak, 1991). The two regenerants tested for 7 IX cycles were 8% NaCl and 7.5% NaCl + 0.5% NaOH (pH=13). Sodium chloride only solution significantly outperformed the high pH regenerant; however, after 7 IX cycles, percent removal of NH_4-N during regeneration was only 17% less for 7.5% NaCl + 0.5% NaOH in comparison to 8% NaCl. Reduced removal compared to 8% NaCl may be due to excessive pH of this solution causing changes to the zeolite surface that reduced NH_4-N exchange; therefore, for the next set of batch tests, the NaOH concentration was decreased.

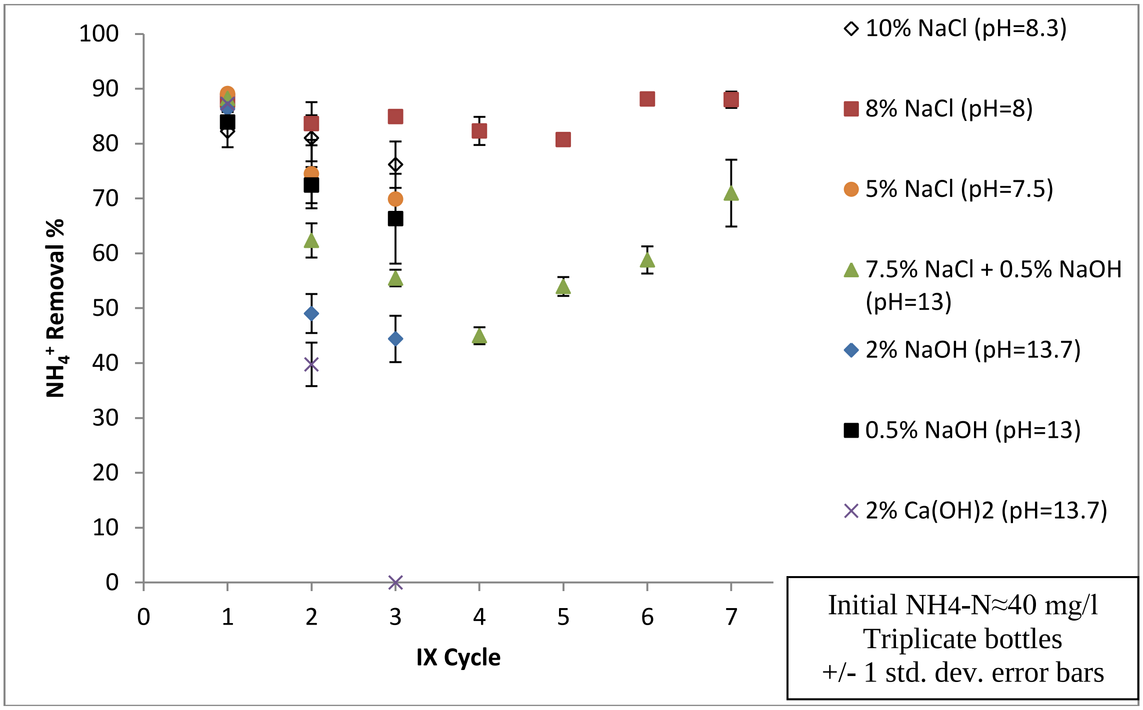

Figure 12: NH_4-N removal by clinoptilolite in NH_4Cl solution vs IX cycle

3.1.2 Zeolite Regeneration for Ammonium Only Batch Testing

Regenerant NH_4-N concentration in regeneration brine was the second parameter of interest for NH_4-N only exchange with clinoptilolite. Regenerant concentration was nearly identical between the 3 NaCl only solutions after 3 cycles, as shown in Figure 13. NH_4-N concentration in the 0.5% NaOH solution was greater than the 2% NaOH solution, which may be attributed to the lower IX performance. As with IX, 7.5% NaCl + 0.5% NaOH resulted in slightly worse performance than 8% NaCl with respect to regenerant NH_4-N concentration. Reduced concentration can be attributed to less exchange of NH_4^+ and therefore less to be desorbed during regeneration. Based on the regeneration and IX results, the NaOH concentration should be decreased if attempting to utilize a high pH solution. The salt concentration should be 8% NaCl or less in order to reduce chemical use.

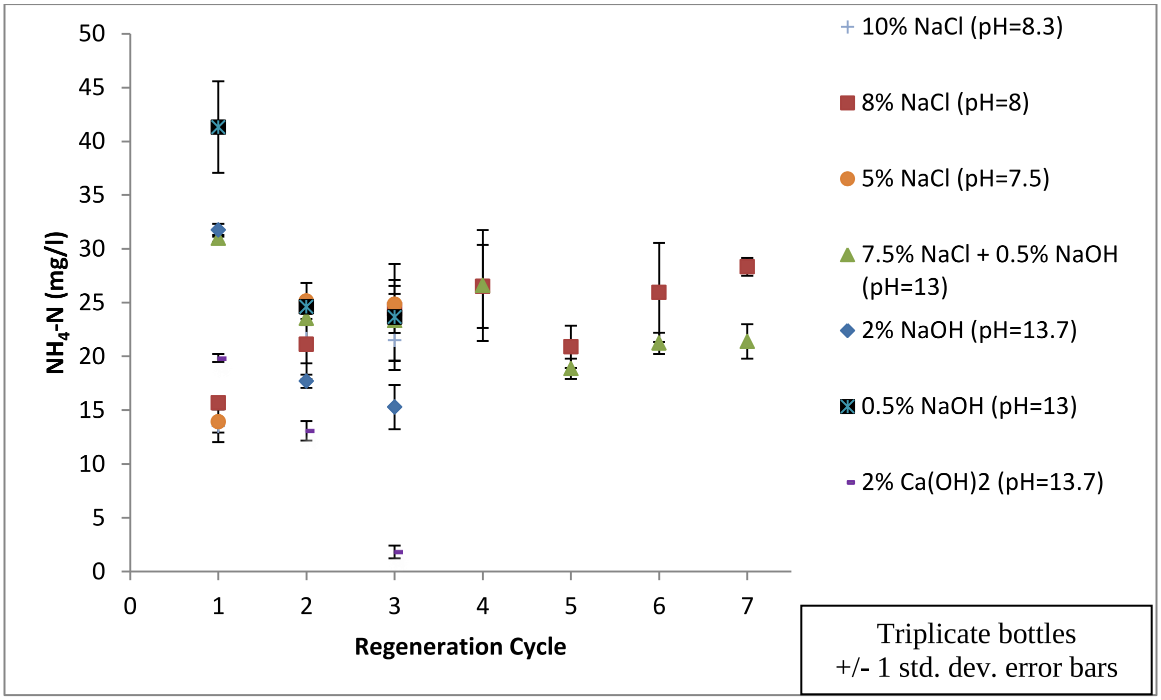

Figure 13: Regenerant NH_4-N concentration (NH_4^+ only test) vs. regeneration cycle

3.1.3 Zeolite Ion Exchange Batch Testing with Mixed Cation Solution

In order to evaluate NH_4^+ exchange in the presence of other cations and revise the set of regenerants tested, a mixed cation batch test was conducted. As before, the goal was to evaluate each regenerant's effect on long-term IX capacity and N desorption. A set of four regenerants were tested in triplicate using clinoptilolite as the media for removal of NH_4^+ from a mixed cation solution. As stated in the methods, mixed cation solution contained Ca^{2+}, Mg^{2+}, K^+, Na^+, and NH_4^+. As with the NH_4-N only batch tests, IX capacity in each cycle was the parameter of interest. Results for 5 IX cycles are displayed in Figure 14 as well as the initial ion concentrations. Results showed that after 3 IX cycles there was no significant difference in using 8% NaCl, 7.5% NaCl (pH=12), or 0.1% NaOH. However, by IX cycle 5, 7.5% NaCl (pH=12) and 8% NaCl were more effective than 0.1% NaOH and 0.1% $Ca(OH)_2$ based on +/- one std. dev. A student's t-test was performed to show statistical dissimilarity, the results of which are in Table A3. After 5 IX cycles there was no statistically significant difference in clinoptilolite performance when regenerated with 8% NaCl (pH=8) or 7.5% NaCl (pH=12). The conclusion is that at a pH of 12, clinoptilolite is successfully regenerated without attrition of the surface.

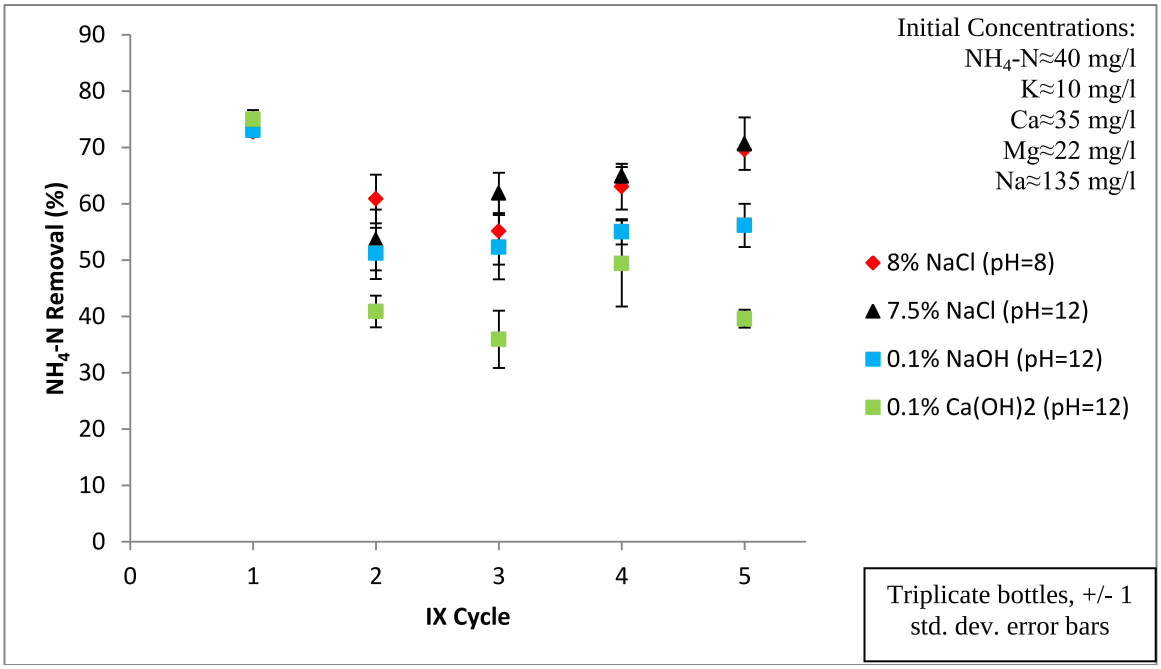

Figure 14: Removal of NH_4-N (mixed cation solution) vs IX cycle

Selectivity of clinoptilolite for NH_4-N exchange over other cations was determined in order to estimate each cation's impact on total NH_4-N exchange capacity.

The parameter used to determine selectivity is called the separation factor and is calculated using Equation 4.

$$\alpha_{\frac{NH_4-N}{M^+}} = \frac{Y_{NH_4-N} * X_{M^+}}{X_{NH_4-N} * Y_{M^+}} \qquad \text{Equation (4)}$$

Where,

$\alpha_{NH4\text{-}N/M+}$= Separation factor of NH_4-N versus a cation

X=Mass of ion in solution (eq)

Y=Mass of ion exchanged onto solid (eq)

M^+=Cation

Separation factors for NH_4-N in relation to Ca^{2+}, Mg^{2+}, K^+ and Na^+ are displayed in Table 4; saturation of exchange sites with Na^+ was assumed in order to enable the calculation (1.85 meq/g solid). For the solutions found to be most effective in regeneration, 8% NaCl and 7.5% NaCl (pH=12), the separation factor for NH_4-N/ Ca^{2+} was slightly less than 1 indicating that Ca^{2+} is slightly more preferred. Separation factor for Mg^{2+} with these same two solutions was near 4, indicating a greater preference for NH_4-N. For K^+, the separation factor was essentially 0, which indicates that K^+ is significantly preferred over NH_4-N by the media. The separation factor for Na^+ is near 1; however, Na^+ ions are being released from the surface since the surface is nearly saturated with Na^+. From these results, the conclusion can be drawn that Ca^{2+} and K^+ concentration in water will significantly affect NH_4-N exchange; however, Na^+ and Mg^{2+} concentration will not.

Table 4: Average separation factor for NH_4^+ during IX cycle 3 and 4.

Separation Factor[1]	Regenerant		Preferred Cation	
	8% NaCl	7.5% NaCl (pH 12)	8% NaCl	7.5% NaCl (pH 12)
$\alpha,_{NH4\text{-}N/Ca}$	0.98	0.78	Ca^{2+}	Ca^{2+}
$\alpha,_{NH4\text{-}N/Mg}$	4.09	3.59	NH_4^+	NH_4^+
$\alpha,_{NH4\text{-}N/K}$	0.00	0.00	K^+	K^+
$\alpha,_{NH4\text{-}N/Na}$	0.97	1.02	Na^+	NH_4^+

3.1.4 Zeolite Regeneration for Mixed Cation IX Batch Tests

Regenerant NH_4-N concentration for each IX cycle was measured in order to determine the recovery potential. Figure 15 displays the results for each IX cycle by type of regenerant. Regenerants containing NaCl and NaOH were similar through 4 regeneration cycles, but after 5 cycles, 8% NaCl and 7.5% NaCl (pH=12) resulted in the greatest concentration and were not statistically different. After 5 cycles, regenerant concentration was about 70% of the initial sample concentration (40 mg/l NH_4-N) for 8% NaCl and 7.5% NaCl (pH=12). Calcium hydroxide performed poorly in regeneration especially during cycle 2 and 3. According to the data in Figs. 9 and 10, the two NaCl solutions outperformed the 0.1% NaOH and 0.1% $Ca(OH)_2$ solutions.

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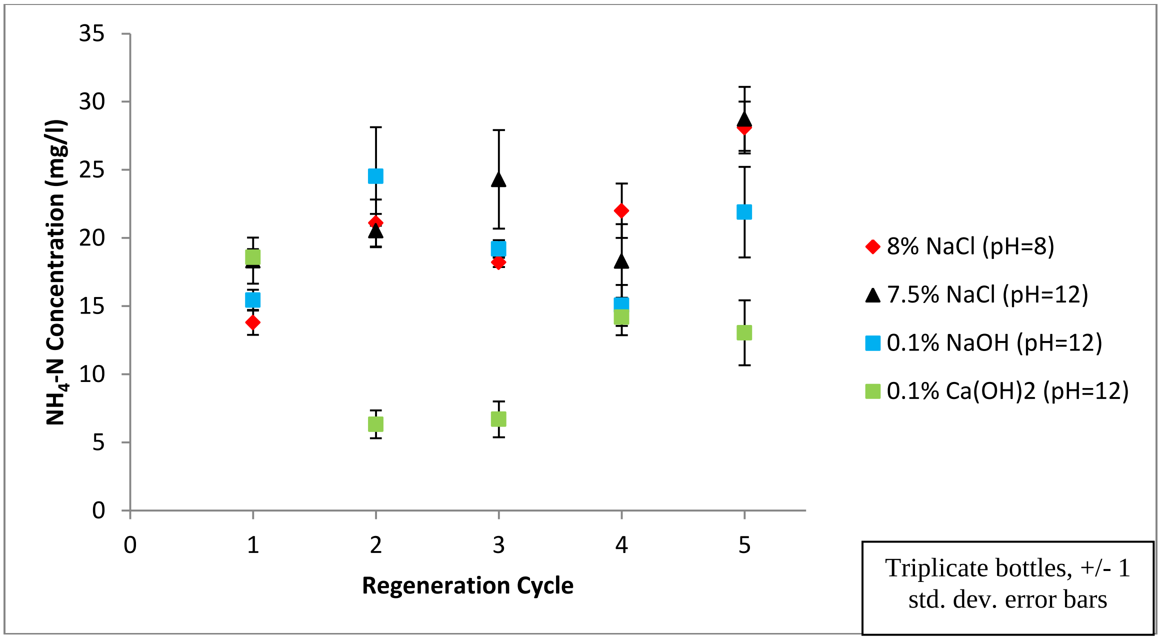
[1] Separation factor>1: NH_4^+ preferred, separation factor<1:other cation preferred



Triplicate bottles, +/- 1 std. dev. error bars

Figure 15: Regenerant NH_4-N concentration (mixed cation test) vs regeneration cycle

3.2 Phosphate Ion Exchange Batch Testing

In order to evaluate PO_4-P removal with various media and then select media for column testing, batch testing was conducted. The first PO_4-P batch testing was conducted with four media, including: Dowex WBA-2, Dowex M4195, LayneRT™, and AA weakly acidic (AA_{wa}). PO_4-P only tests were conducted in order to compare uptake of PO_4-P among resins without the presence of competing anions. Results are displayed in Table 5. Essentially all PO_4-P was removed with Dowex WBA-2, LayneRT™, and AA_{wa}. However, Dowex M4195 only removed about 17% of PO_4-P. This result is because the surface of Dowex M4195 is designed for preparation as a ligand exchange resin through loading of metals on the surface. Regeneration of the resins was conducted using 6% NaCl at pH=10. This solution was found to desorb almost all PO_4-P for Dowex WBA-2 and Dowex M4195, but essentially none for LayneRT™ and AA_{wa}.

Table 5: Phosphate only batch IX (triplicate bottles)

Ion Exchange	**Dowex WBA-2**	**Dowex M4195**	**LayneRT™ (PhosX)**	**AA weakly acidic**	**Control (Glass adsorption)**
Final PO_4-P, Avg. (mg/l)	0.006	2.4	<0.006	0.02	2.9
Sorption (mg/g)	0.29	0.05	0.29	0.29	
Removal (%)	100	18	100	99	

Following PO_4-P only testing, mixed anion exchange was tested to determine the effect of competing ions on PO_4-P uptake; initial and final anion concentrations are displayed in Table 6. Dowex M4195 and AA_{wa} results were slightly affected as percent PO_4-P removal decreased from 17 to 12 and 99 to 95%, respectively. However, this is not a substantial change considering AA_{wa} was still capable of removing 95% of PO_4-P in the presence of large concentrations of other anions. LayneRT™ was not affected by the presence of other anions as removal of PO_4-P was essentially 100%. As expected, Dowex WBA-2, a non-PO_4-P selective resin, was significantly affected by the presence of other anions as PO_4-P removal decreased from almost 100% to 64%. This is caused by a lack of PO_4-P specific binding sites on the resin.

Sulfate, alkalinity, and chloride uptake/release were investigated, as shown in Table 5; these anions are expected to be found in the most significant concentration in municipal secondary effluent. Chloride was released in 3 of the media with the exception of LayneRT™ which resulted in some uptake of chloride. Almost 100% of SO_4^{-2} was removed by Dow-WBA2 whereas LayneRT™ removed just 13%; selectivity towards P removal by LayneRT™ will reduce the number of regeneration cycles required in comparison to Dow-WBA2. Removal of alkalinity, mostly in the form of bicarbonate, was greatest in Dow-WBA2, the non-selective media. Sulfide and nitrate concentrations were lower than expected in the controls and therefore difficult to detect.

Regeneration of the media was conducted using three different brine solutions based on the literature; solutions used are listed in Table 7. The regeneration test was performed to determine P desorption potential with the revised solutions based on the first batch test and literature. Regeneration was only slightly successful with Dowex M4195, LayneRT™, and AA_{wa}; desorption of PO_4-P was 31%, 31%, and 38%, respectively. Results for LayneRT™ desorption were surprising as previous work has shown >90% desorption of PO_4-P in column tests; however, this may be due to the difference in kinetics between batch and column testing (Blaney *et al.*, 2007). Complete PO_4-P desorption was achieved for Dowex WBA-2. Control and final pH values illustrate the uptake of OH^- ions onto the media surface during regeneration. Clearly there is uptake of OH^- ions in Dowex WBA-2 and Dowex M4195; however, for the other two media, results are inconclusive. Knowing the pH change during regeneration is necessary for estimating the amount of chemicals that will be required to adjust pH of the regenerant before P recovery or disposal. Dow WBA-2 was not tested further due to its lack of selectivity towards PO_4-P. Dowex M4195 was only tested in the metal-loaded (Cu, Fe, Al, or Cu & Fe) form for the rest of the study.

Table 6: Final solution characteristics in mixed anion solution batch IX (triplicate averages)

Ion Exchange	PO_4-P	Cl^-	SO_4-S	Alkalinity	HCO_3^- (Assuming all Alk. is HCO_3^-)	pH after IX
	mg/l	mg/l	mg/l	mg/l as $CaCO_3$	mg/l	
Dowex WBA-2	1.2	65	<0.8	119	72	7.1
Dowex M4195	2.9	70	39	0	0	2.6
LayneRT™ (PhosX)	<0.006	48	14	96	59	7.0
AA weakly acidic	0.18	70	4.4	112	68	7.6
Control (Glass adsorption)	3.3	55	16	136	83	7.4

Table 7: Mixed anion regeneration test (triplicate averages)

Regeneration	PO_4-P	Initial regen. pH	Final regen. pH	Regenerant	P Desorbed
	mg/l				%
Dowex WBA-2	2.6	10.1	9.6	5% NaCl, pH=10	114
Dowex M4195	0.14	10.1	9.3	5% NaCl, pH=10	31
LayneRT™ (PhosX)	1.0	13.4	13.4	2% NaCl, 2% NaOH	31
AA weakly acidic	0.9	13.4	13.3	2% NaOH	38

In order to determine maximum sorption of PO_4-P in conditions that were not P limited, anionic IX media were tested in a spiked PO_4-P batch test containing 100 mg/l PO_4-P. An excess PO_4-P concentration, greater than the exchange potential, was used in order to determine maximum exchange capability. Eight media were tested and results from the test are listed in Table 8 in order of greatest PO_4-P removal to least. Removal of

PO_4-P with Dow-Cu was significantly ($p \leq 0.014$) better in terms of IX performance than all other resins. A student's t-test was conducted to determine statistical difference between media; a p-value of less than 0.05 indicates statistical difference with 95% confidence. The student's t-test results for spiked PO_4-P IX are in Table 9. LayneRT™ and Dow-FeCu were found to perform similarly and their performance was only about 12-16% less than Dow-Cu. Statistics also show that Dow-NAB-Cu and Dow-HFO IX performance are similar. PO_4-P uptake with the two activated alumina media was less than 50% of Dow-Cu and Dow-FeCu. Applying $KMnO_4$ and $Al_2(SO_4)_3$ in two steps was the most successful IX resin loaded with Al; however, as shown in Table 6, this resin performed at less than a third the capacity of Dow-Cu. Based on batch testing, the three top performing resins were identified for use in column tests; these media were Dow-Cu, Dow-FeCu, and LayneRT™.

Table 8: Spiked phosphate batch IX (triplicate bottles)

Resin	**Removal**	**PO_4-P**
	%	mg/l
Dow-Cu	76	24
DOW-FeCu	64	36
LayneRT™	60	41
Dow-NAB-Cu	53	47
DOW-HFO	52	49
AA neutral	32	67
AA basic	28	72
Dow-Mn-Alum	23	78

Table 9: Student t-test p-values for spiked phosphate IX

	Dow-Cu	DOW-FeCu	LayneRT™	DOW-NAB-Cu	DOW-HFO	AA neutral	AA basic
DOW-FeCu	0.0014						
LayneRT™	0.0008	0.016					
DOW-Cu	0.0001	0.0003	0.0033				
DOW-HFO	0.0002	0.0011	0.0066	0.18			
AA neutral	0.0000	0.0000	0.0000	0.0000	0.0004		
AA basic	0.0000	0.0000	0.0000	0.0000	0.0001	0.013	
DOW-Mn-Alum	0.0000	0.0000	0.0000	0.0000	0.0000	0.0004	0.0022

For comparison of desorption capabilities of each resin, regeneration of the media used in spiked PO_4-P batch testing was conducted. Regenerants were selected either based upon solution used in previous research, as listed in Table 1, or utilizing salt solution at a neutral pH; solutions for each media are listed in Table 10. Regenerant concentration was greatest for Dow-Cu; however, the Dow-FeCu had the greatest percent desorption. Regeneration of Dow-NAB-Cu and AA neutral (AA_n) desorbed less than 40% of PO_4-P. Dow-HFO regeneration was ineffective as only 8% was desorbed; the strong binding between iron and PO_4-P requires a higher pH to reverse. A student's t-test was conducted on percent desorption and results are found in Table A6. There was no statistical difference between Dow-Cu and Dow-FeCu. Dow-Cu removed the most P, but requires acidic regenerant (pH=4.3). However, for Dow-Cu batch tests, the final regenerant pH is neutral which suggests that little pH adjustment will be necessary prior to struvite precipitation. LayneRT™ can be purchased pre-prepared and has the 3rd greatest P removal, but requires a strong basic solution (pH=14) to regenerate. The data led to the conclusion that Dow-FeCu is best of the tested resins as it has a large IX capacity, large percent desorption and does not require acid or caustic chemical additions to the regenerant.

Table 10: Regeneration performance for spiked P test (triplicate bottles)

Resin	Regenerate	PO_4-P	Desorption	Final pH
		mg/l	%	
DOW-Cu	6% NaCl pH=4.3	46	60	7.2
DOW-FeCu	6% NaCl pH=8	42	65	7.6
LayneRT™	2% NaCl + 2% NaOH	30	49	13.4
Dow-NAB-Cu	6% NaCl pH=4.3	20	38	6.4
AA basic	6% NaCl pH=9.5	14	53	9.0
AA neutral	6% NaCl pH=7.5	10	31	8.2
DOW-HFO	6% NaCl pH=8	4	8	6.3

3.3 Wastewater Characterization

Column tests were conducted using actual wastewater to account for biological activity and dissolved organic carbon. Secondary clarifier effluent from South Shore Wastewater Treatment Plant was collected and analyzed to determine concentrations of cations, anions, BOD, and organic P (orgP). The wastewater contained 1.5 mg/l NH_4-N and 0.2 mg/l PO_4-P; complete characterization is given in Table A8. Based on the anaerobic treatment mass balances for N and P in Figs. 3 and 4, expected of TKN and TP were 42 mg/l and 3.5 mg/l, respectively, with most of the nutrients in the form of NH_4^+ and PO_4^{-3}, respectively. As a result, the nutrient concentrations were supplemented to about 32 mg/l NH_4-N and 4-6 mg/l PO_4-P. There is 4.5 mg/l NO_3-N in the secondary effluent which would not be expected in AnMBR permeate since there is no aeration step to nitrify NH_4^+ to NO_3^-. The BOD_5 of the wastewater is 12 mg/l which is comparable to expected AnMBR permeate quality (Kim *et al.*, 2011). Cl^-, alkalinity, SO_4-S, K^+, Ca^{2+}, Mg^{2+}, and Na^+ were found in significant concentrations (all were greater than 8 mg/l). In anaerobic wastewater, much of the sulfate would be present as sulfide as a result of biologically mediated reduction. The only heavy metals detected in the wastewater were aluminum and copper. After nutrient dosing and before pumping sample into the columns, the wastewater was passed through a 1.5 μm filter to remove suspended particles that would not be present in AnMBR permeate. This resulted in removal of about 0.1 mg/l TP and likely some BOD_5 and TKN.

A strong potential for inorganic fouling was determined using the Langelier Saturation Index. Influent wastewater to the IX system has a pH of 7.6. At this pH HCO_3^- will exist in significantly greater concentrations than CO_3^{-2} and therefore CO_3^{-2} is assumed to be zero. In addition, all alkalinity is assumed to be in the HCO_3^- form since OH^- concentration is minimal at neutral pH and no other significant source of alkalinity is expected. Using eqn. 1, the first 2 terms cancel out since $CO_3^{-2}\approx 0$; the first 2 terms become -log(<<0.0001)+log(<<0.0001). Using the wastewater Ca^{2+} and alkalinity concentration in mol/L, the $pH_{saturation}=5.3$ and therefore the LSI=2.3. An LSI between 1 and 3 is considered a strong to very strong fouling potential.

3.4 Removal of Phosphate in Lab-Scale Ion Exchange Columns

An anion exchange column was tested as the first step in nutrient removal from secondary effluent dosed with nutrients. Column testing was conducted as full-scale operation would be in column mode. The first media tested was LayneRT™, a commercially available iron-loaded resin that was proven effective for P removal in batch testing. Effluent, average influent and breakthrough PO_4-P concentration are displayed in Figure 16. Influent anion concentrations are also provided as these impact PO_4-P exchange capacity. However, it is important to note that nearly no NO_3^- is expected in AnMBR permeate and most sulfur will be reduced from SO_4^{-2} to HS^- in the AnMBR; therefore, secondary effluent differs from AnMBR, but is the most similar alternative without operation of the AnMBR. Influent and effluent pH for the column was 7.6 and 7.2, respectively. The column was capable of treating 500 BV of wastewater containing 4 mg/l PO_4-P before effluent PO_4-P exceeded 0.075 mg/l. Breakthrough of 0.075 mg/l PO_4-P was selected as strict regulations begin to be implemented nationwide. Total mass of P exchanged before breakthrough was 73.9 mg; this is equivalent to 2000 mg P/L_{BV}. Volume of resin including the material and void space is denoted as L_{BV}. This number provides design criteria for PO_4-P IX beds with LayneRT™; 2000 mg P/L_{BV} explains that a liter of LayneRT™ BV will remove 2 g of P before column breakthrough occurs. The results for this column are similar to those by Sengupta and Pandit (2011) that found that LayneRT™ could treat 625 BV of 2.75 mg/l P solution before breakthrough.

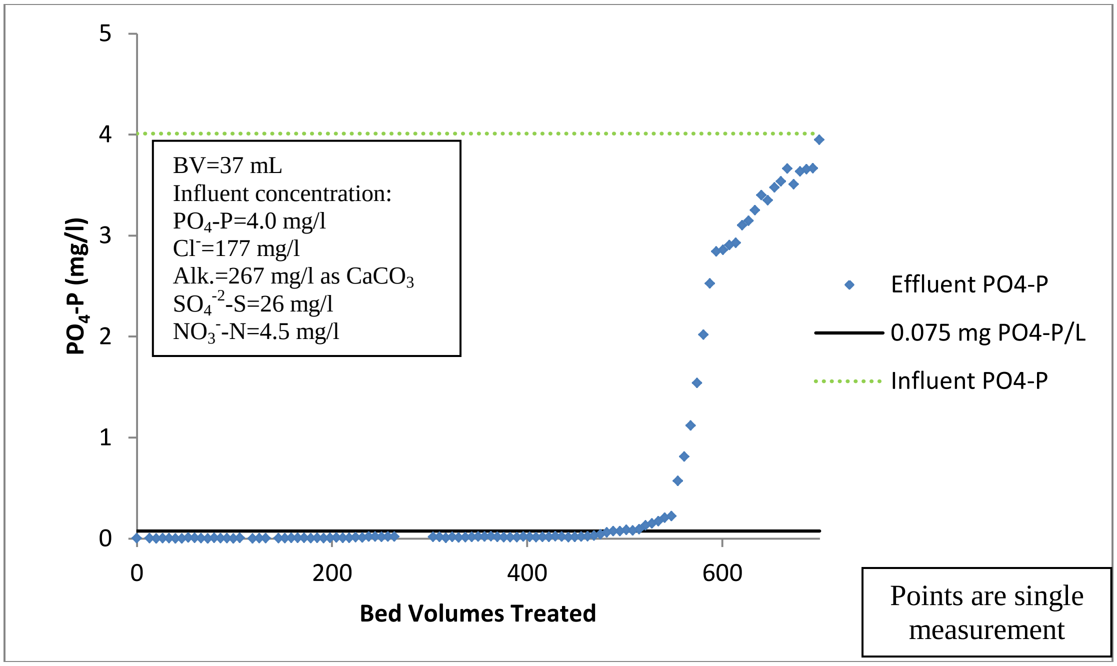


Figure 16: LayneRT™ column effluent PO_4-P vs BV treated.

Dow-Cu was tested in a column for comparison to LayneRT™ since it resulted in the greatest PO_4-P removal during spiked PO_4-P batch testing. Influent PO_4-P concentration was slightly greater, 5.6 mg/l vs. 4.0 mg/l, for Dow-Cu than the LayneRT™ column. Effluent PO_4-P data is depicted in Figure 17. Influent and effluent pH were 8.7 and 8.1, respectively; the pH was greater than expected AnMBR permeate, but was not extreme. Breakthrough occurred at about 82 BV of treated wastewater resulting in about 16.8 mg of P exchange after 82 BV. Therefore, Dow-Cu has a PO_4-P exchange capacity prior to breakthrough of 455 mg PO_4-P/L_{BV}. This resin has less than 25% of the capacity of LayneRT™ which contradicts batch test results. However, these results are similar to work by Kumar *et al.* (2007) in which capacity of LayneRT™ was found to be approximately 5 times that of Dow-Cu. The benefit to Dow-Cu is that regeneration requires an acidic solution (pH=4.3) that may not require as much pH adjustment as LayneRT™ which uses a regenerant with pH>14.

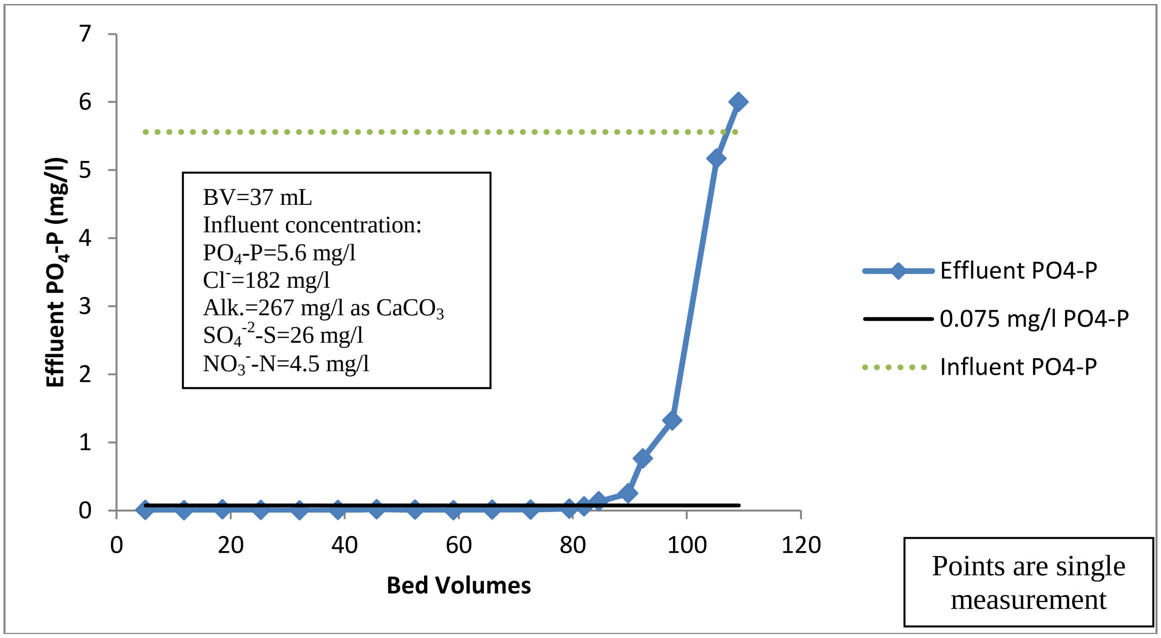


Figure 17: Dow-Cu cycle 1 column effluent PO_4-P vs BV treated

The capacity of Dow-Cu was much less than LayneRT™ and the influent pH for Dow-Cu cycle 1 was about 8.7; in order to test whether the pH affected capacity, a second IX cycle was conducted. In addition, a second IX cycle provided the change in IX capacity between cycle 1 and 2 which is variable depending on P desorption percent and Cu^{2+} leaching. In this test, the influent pH was reduced to 7.4 and the influent PO_4-P concentration was 5.9 mg/l; effluent pH was 7.1. Effluent PO_4-P data is shown in Figure 18. In the second cycle, breakthrough of PO_4-P occurred at about 68 BV; the total exchanged P during the first 68 BV was 14.7 mg. Exchange capacity was reduced by 12% indicating insufficient regeneration of the resin, irreversible fouling, or copper leaching. Regeneration of the resin will be discussed in the next section, including % P desorption and regenerant Cu leaching. Previous work has claimed the resin can be utilized for more than 100 cycles without significant loss in capacity (Zhao and Sengupta, 1998).

Copper leaching was found to be significant in both Dow-Cu column runs. Four samples were taken from each IX cycle to determine effluent Cu concentration; metal leaching data from anion IX runs are in Table A9. In both cases effluent Cu was around 3-3.5 mg/l initially and then reduced to about 1 mg/l at the end of the test. Copper leaching may be more significant in initial column runs due to weakly bonded Cu or could be attributed to difference in preparation methods. For example, in Zhao and Sengupta (1996) the resin is dried at 45 °C, whereas, in our study it is dried at 35 °C. In contrast, no metals were found to leach in significant concentrations from the LayneRT™ column. Therefore, capacity of LayneRT™ should not change significantly due to loss of surface ions as could be the case for Dow-Cu.

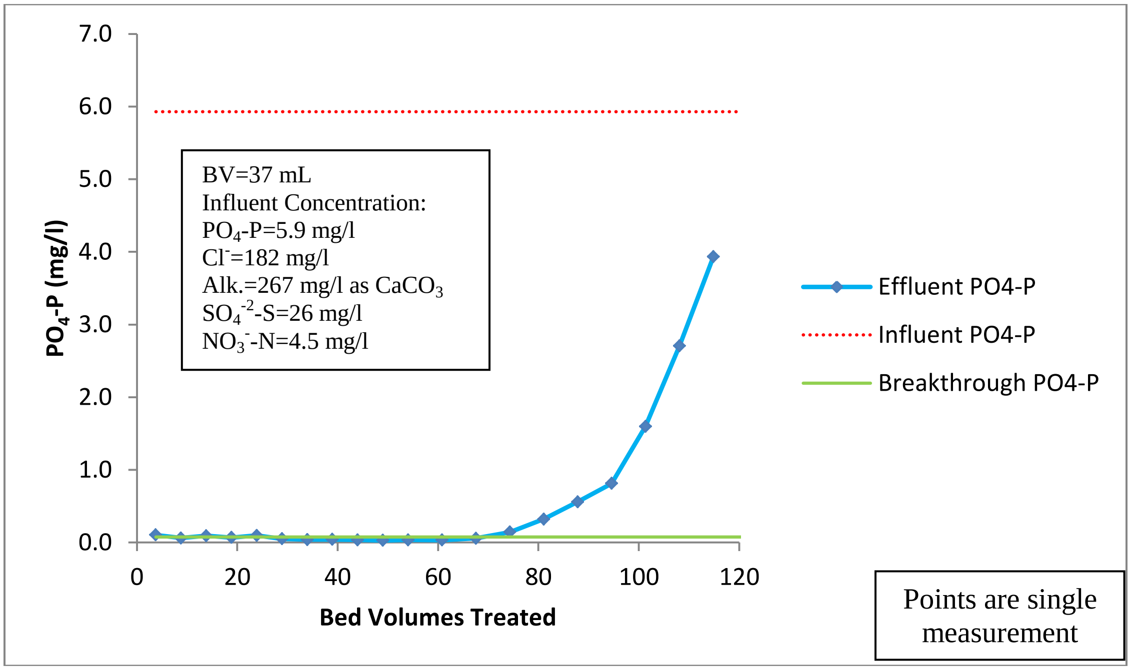


Figure 18: Dow-Cu cycle 2 column effluent PO_4-P vs BV treated

Dowex M4195 resin loaded with Fe and Cu (DowFeCu) was tested in column mode with an influent PO_4-P concentration of 6.7 mg/l. Breakthrough of this resin occurred at 237 BV of wastewater treated as shown in Figure 19. P exchanged during this period was 55.3 mg which is 1490 mg P/L_{BV}. This is essentially 75% of the capacity of LayneRT™, a more promising result than that of Dow-Cu. Previous work showed that the capacity of Dow-HFO-Cu was twice as great as LayneRT™ (Sengupta and Pandit, 2011). Upon further reading, it was discovered that Dow-HFO-Cu was prepared without the acid and base treatment step and therefore, the author of the present work denoted the acid and base treated resin as Dow-FeCu to distinguish the two (Sengupta, 2013). Preparation of Dow-FeCu requires four steps whereas LayneRT™ can be purchased ready-to-use; however, data indicate efficient regeneration of Dow-FeCu at a neutral pH which would provide cost savings in operation through reduced acid addition for pH adjustment. Preparation of Dow-HFO-Cu instead of Dow-FeCu will reduce the steps required and should improve exchange capacity of the resin as the acid and base treatment likely removes some hydrated ferric oxide (HFO) particles from the resin surface.

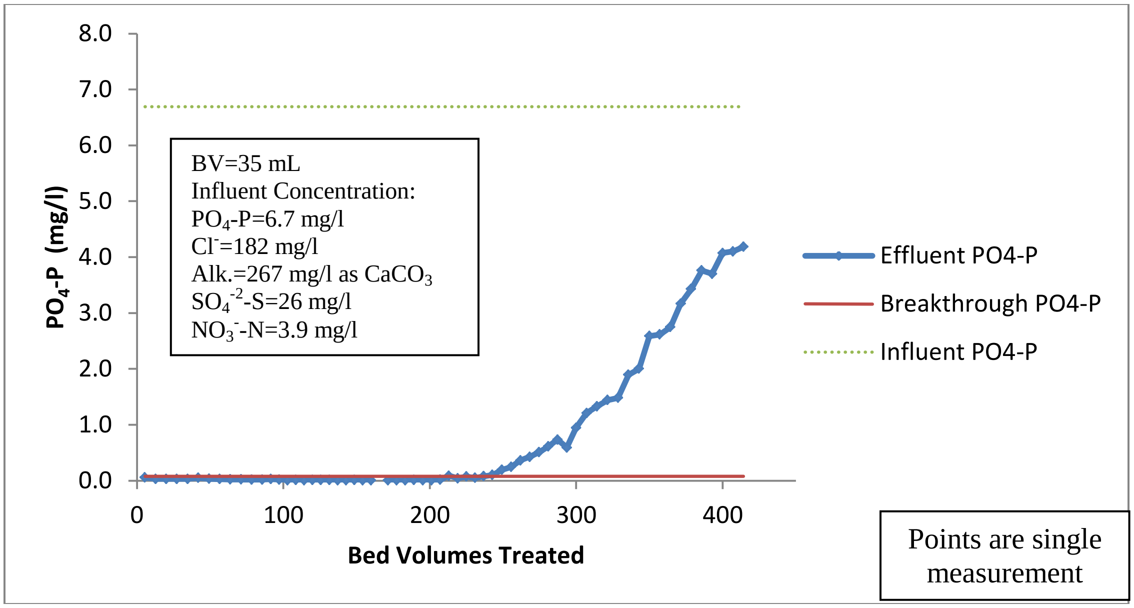


Figure 19: Dow-FeCu effluent PO_4-P concentration vs BV treated

3.5 Desorption of Phosphate from Lab-Scale Ion Exchange Columns

Since the goal is not just P removal, but P recovery, desorption of P from the media is important. In order to test the P desorption, regeneration of the IX columns was conducted. Regeneration of the LayneRT™ IX column was accomplished with 2% NaCl + 2% NaOH (pH=14). Total desorption of PO_4-P was 78 mg or 89% of influent P exchanged. Effluent P versus BV passed is displayed in Figure 20. As illustrated, most of the PO_4-P desorption occurred within the first 6 BV. Previous work claimed similar regeneration results of >90% PO_4-P desorption in less than 10 BV. With a substantial portion of PO_4-P remaining on the resin, exchange capacity during cycle 2 is likely to be reduced. A long-term study is necessary to determine the impact on capacity after many IX cycles; the resin has been tested for 10 cycles, however, data has not been published or only partial regeneration was conducted (Martin *et al.*, 2009; Sengupta and Pandit, 2011). Using regression curves, the estimated concentration of PO_4-P after 4 BV was calculated. If 4 BV of regenerant were used, the concentration of PO_4-P would be 490 mg/l. After 4 BV, only 82% of PO_4-P is desorbed; however, the loss in capacity may not be an issue as regenerating more often with less solution is potentially less costly than regenerating to complete desorption each cycle. LayneRT™ regenerant cation concentrations from the first 250 mL of regenerant are listed in Table A10. Iron leaching was not significant; however, aluminum leaching was 155 mg/l. High concentrations of Al^{3+} will cause issues when precipitating struvite as aluminum hydroxides and aluminum phosphates will form which are not as amenable to fertilizer application due to limited bioavailability of P and Al^{3+} toxicity (Mossor-Pietraszewska, 2001; Peret *et al.*, 2011). Measured PO_4-P concentration was 536 mg/l which is slightly greater than the estimated value, indicating that desorption was greater than calculated. The concentration factor for P is greater than 130 times. LayneRT™ PO_4-P exchange and desorption performance is excellent, but requires extreme pH (14) to regenerate.

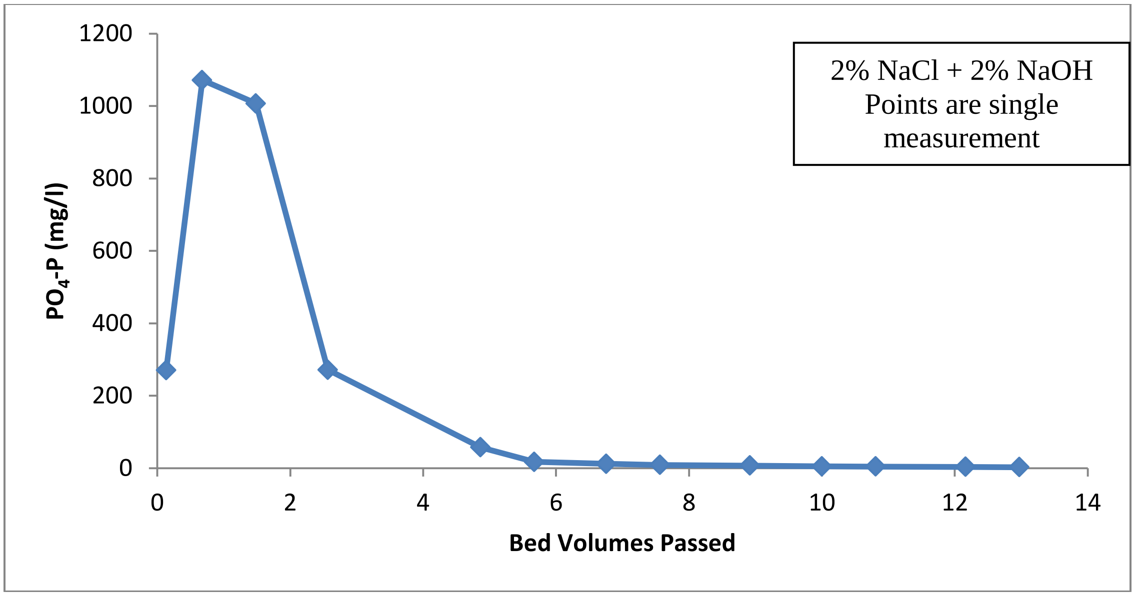


Figure 20: LayneRT™ regeneration effluent PO_4-P vs BV passed

Regeneration of Dow-Cu was performed following both IX cycles for comparison; desorption may change between cycles if P is not completely removed during the previous regeneration or there is a change in the P removed during IX. Regeneration of Dow-Cu was similar for both cycles; effluent PO4-P concentration versus BV passed is shown in Figure 21. The regenerant was 6% NaCl at a pH of 4.3. Total PO_4-P desorption was 97% and 90% during cycle 1 and 2, respectively. Effluent PO_4-P in the initial regenerant was much greater during IX cycle 1 than 2; however, as the test progressed, the effluent concentration became more similar. In both cycles, PO_4-P concentration in the first 1.5 BV of regenerant is about 325-350 mg/l. Percent PO_4-P desorption after 1.5 BV is 88% and 83% for regeneration cycle 1 and 2, respectively. Just as with LayneRT™, complete desorption of the resin is unnecessary as it requires large volumes of chemical solution to desorb the last 10-15% of PO_4-P. Data from Table A10 show that measured PO_4-P concentration is about 150 mg/l in the first 4 BV of regenerant for both regeneration cycles. Regenerant effluent pH during the first 4 BV was 9.90. This is likely caused by uptake of hydrogen protons by PO_4-P. Copper concentration in the first 4 BV of cycle 1 and 2 regenerant was 7 and 26 mg/l, respectively. For reasons undetermined, copper leaching was much greater during regeneration cycle 2. A possible solution for copper leaching is to add 10-30 mg/l Cu^{2+} to the regenerant in an attempt to limit Cu^{2+} release from the resin; another solution would be to place virgin resin containing at the bottom of the column to capture Cu^{2+}. Desorption of Dow-Cu is effective with less volume of solution than LayneRT™; however, regeneration would be necessary more often and the concentration factor is about 58 instead of 130. This resin provides a brine PO_4-P solution with a pH ideal for struvite precipitation.

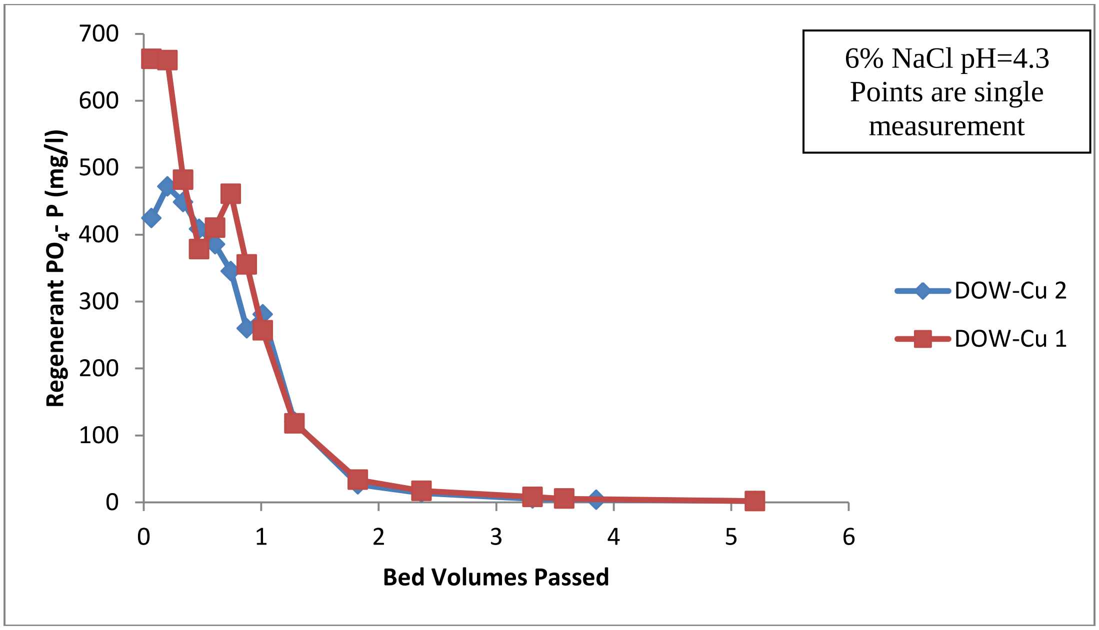


Figure 21: DOW-Cu regenerant PO_4-P concentration vs BV passed during cycle 1 and 2

Regeneration of Dow-FeCu was conducted for comparison to Dow-Cu and LayneRT™. Dow-FeCu was regenerated using 6% NaCl at a pH of 8 based on successful P desorption during batch testing. Greater than 90% desorption of PO_4-P was accomplished with 5 BV and within the first 1.3 BV, 83% PO_4-P desorption occurred. Peak regenerant concentration was 1500 mg/l PO_4-P and the concentration in the first 4 BV was 506 mg/l; regeneration eluate PO_4-P concentration vs. BV treated is depicted in Figure 22. The concentration factor is 76, but would likely be much greater if the influent PO_4-P concentration was only dosed to 4 mg/l instead of 6.7 mg/l. Regeneration eluate pH was 9.6 in the first 4 BV which is within range of typical pH used for operation of struvite precipitation. Leaching of Cu^{2+} was significant with 30 mg/l Cu^{2+} in the first 4 BV of regenerant. Methods to offset the loss of Cu^{2+} should be considered as discussed for Dow-Cu in the previous section. Dow-FeCu provides nearly the same capacity as LayneRT™ with the benefit of regeneration effectiveness at neutral pH. Improving this resin's capacity to match previous research by Sengupta and Pandit (2011) will make Dow-FeCu the optimal resin for PO_4-P IX in municipal wastewater.

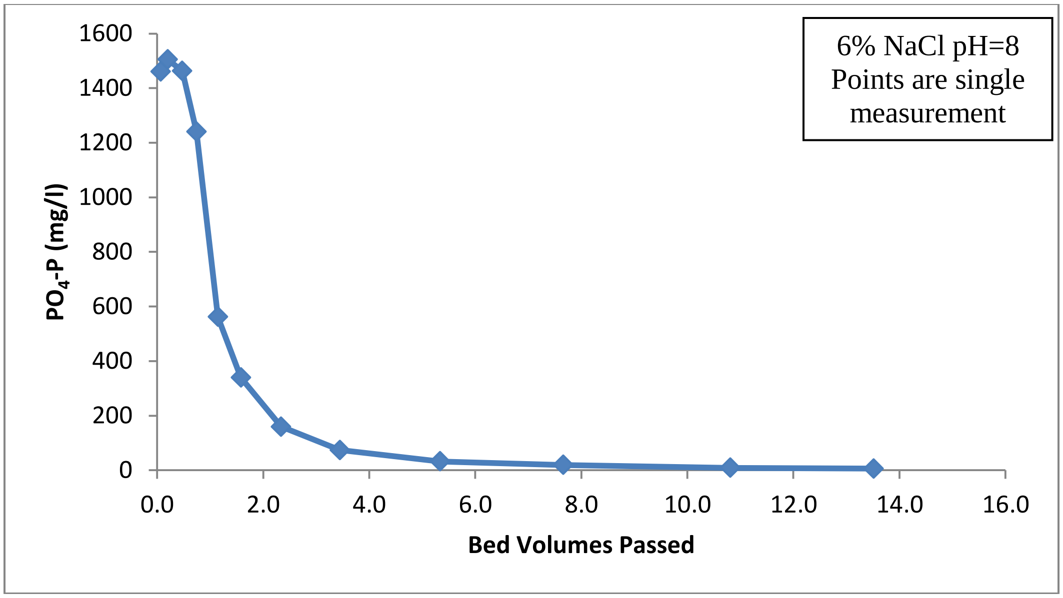


Figure 22: Dow-FeCu regenerant effluent PO_4-P concentration vs BV passed

3.6 Ammonium Exchange in a Lab-Scale Zeolite Column

Zeolite was tested as the cation exchange media for NH_4^+ removal from secondary effluent pre-treated by a column with LayneRT™ media. The column influent was effluent from the LayneRT™ anion exchange column to simulate dual IX for P and N removal. Effluent NH_4-N versus BV treated for IX cycle 1 are depicted in Figure 23. Influent cations are listed in Figure 23 as these concentrations will substantially impact the NH_4-N exchange capacity of zeolite. Breakthrough for zeolite was considered 1.5 mg/l NH_4-N and the column maintained effluent less than this concentration for 128 BV. The exchange capacity prior to breakthrough for zeolite was 4050 mg NH_4-N/L_{BV}. Therefore the exchange capacity in eq-N/L is 0.29 which is within the range of 0.2-0.5 eq/L reported by the USEPA (1993) for wastewater applications. Although the zeolite column reaches breakthrough (effluent NH_4-N>1.5 mg/l or PO_4-P>0.075 mg/l) before

LayneRT™ and Dow-FeCu, complete exhaustion of the zeolite bed (influent NH_4-N=effluent NH_4-N) occurs more slowly following breakthrough. Zeolite media provided treatment for about a quarter of the wastewater that LayneRT™ did, which means that the cation column will require regeneration more often.

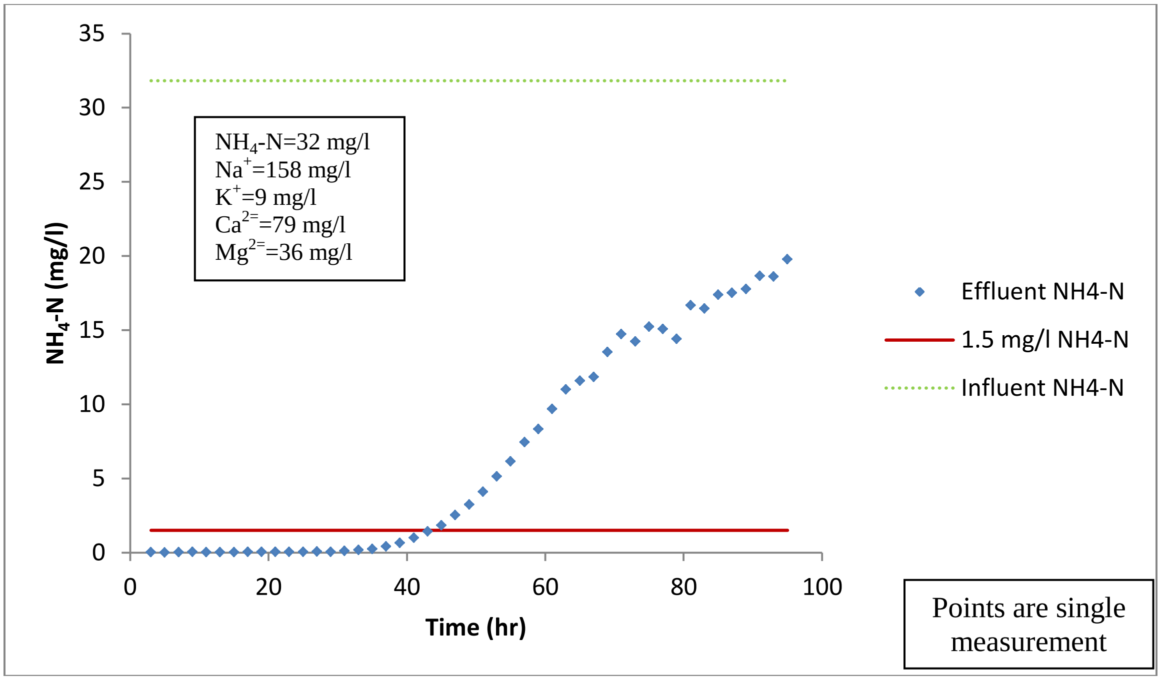


Figure 23: Zeolite column effluent NH_4-N vs BV treated (cycle 1)

The zeolite column was operated for a second cycle following regeneration in order to determine the change in exchange capacity. Cation exchange capacity of the media may change between cycles if complete desorption of N does not occur during regeneration or the material properties are changed by the regenerant. A substantial difference in performance between cycle 1 and 2 occurred; effluent NH_4-N concentration remained around 1 mg/l for the first 184 BV instead of nearly 0 mg/l as was the case in cycle 1; results are shown in Figure 24. This may be attributed to a change in surface characteristics due to the high pH regenerant; however, further studies are necessary. Using a breakthrough of 1.5 mg/l NH_4-N, the column treated 191 BV of wastewater before breakthrough with an exchange capacity of 6190 mg NH_4-N/LBV or 0.4 meq-N/L. NH_4-N exchange capacity was about 50% greater cycle 2. Influent cation concentrations were unexpectedly lower in cycle 2, likely resulting in increased exchange capacity of NH_4-N. In previous work, it was predicted that specific surface area of the mineral increased during the first two regenerations due to expansion of macropores which in turn increased exchange capacity (Turan and Celik, 2003). Treatment of wastewater for many cycles should be conducted to better determine if capacity changes are caused by regeneration or variability of the wastewater cations.

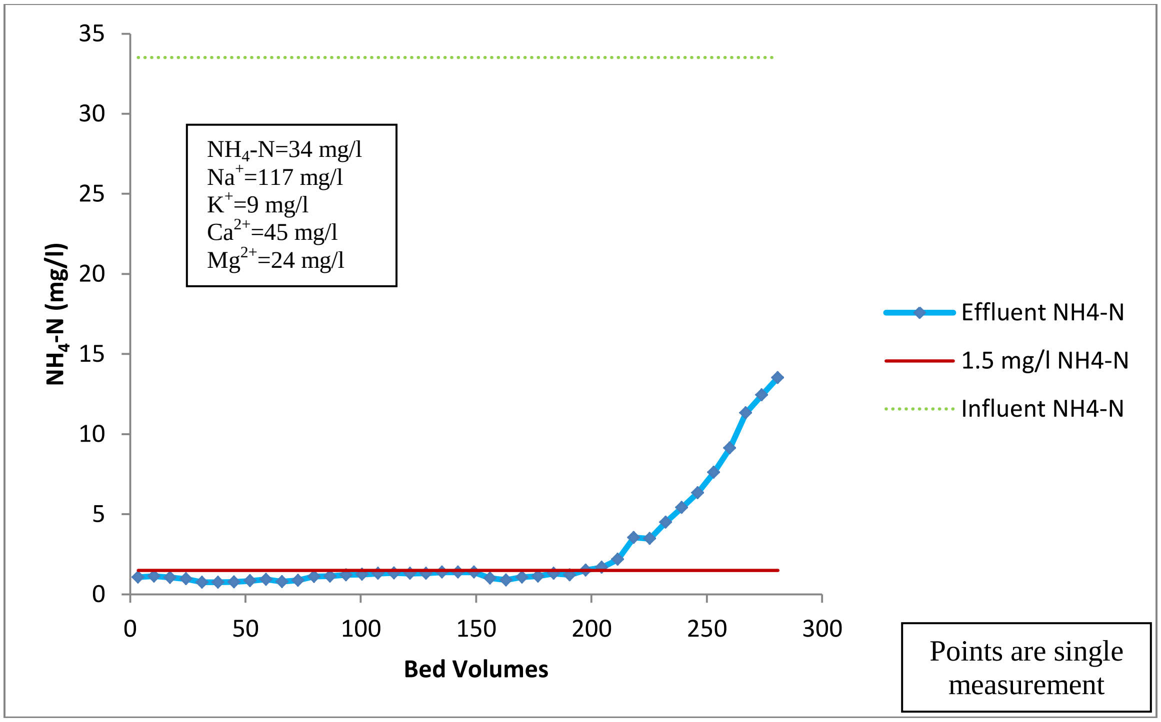


Figure 24: Zeolite column effluent NH_4-N vs BV treated (cycle 2)

Cations in the effluent were tested in order to determine the amount of each ion being exchanged. Design of columns is dependent upon uptake of other cations; the more K^+, Ca^{2+}, etc. in the wastewater, the more media that is necessary. Determining uptake of each cation will determine which cations to consider during design as well as which cations may be desorbed in the regenerant. Metals were measured in every third sample tested for NH_4-N concentration in the zeolite column effluent. Concentrations of K^+, Na^+, Mg^{2+}, Ca^{2+}, and NH_4-N in zeolite column effluent for IX cycle 1 and 2 are found in Figures A1 and A2, respectively. In the first cycle, effluent K^+ concentration equaled influent concentration initially and then rose over time until near equilibrium at which point K^+ was discharged at 4 times the influent concentration. This is likely explained by K^+ attached to the zeolite surface that was not released during preconditioning. However, during the second cycle, K^+ was exchanged until near equilibrium at which point influent equaled the effluent. Therefore difference in preconditioning and regeneration of zeolite greatly impacts the exchange process; these results were also found in batch testing. Magnesium was exchanged for the first 25 BV of cycle 1, but then was not exchanged for the rest of cycle 1 or in cycle 2. Calcium is significantly exchanged early in the IX cycles, but then gradually increases until it is equivalent to the influent. Therefore, Ca^{2+} concentration will greatly impact exchange capacity of NH_4-N, but Mg^{2+} will not. Upon analysis of the metals data, K^+ and Ca^{2+} have the greatest impact on exchange capacity of zeolite.

Heavy metals exchanged onto the zeolite surface were of interest as there is the potential for them to desorb in the regenerant and precipitate in the recovered solids. Most heavy metals were below detection range for this wastewater, as shown in Table

A8. However, Al^{3+} was detectable and according to the data in Figure A3, Al^{3+} is completely exchanged after the first 30 BV of wastewater. The effect on NH_4^+ exchange is minimal due to the low concentration of Al^{3+}; however, in other wastewaters this could become an issue for zeolite NH_4^+ exchange.

3.7 Ammonium desorption during Lab-Scale Zeolite Regeneration

Regeneration of zeolite was conducted to determine the percent desorption of N and to perform subsequent IX. Desorption of N is critical for maintaining N removal during successive IX and capturing N for recovery. Zeolite was regenerated in column mode using 6% NaCl (pH=11) for both regeneration cycles. Regenerant eluate NH_4-N concentration versus BV passed is displayed in Figure 25. Peak NH_4-N concentration during regeneration cycle 2 was almost twice as great as during cycle 1. Total desorption of NH_4-N during cycle 1 was 74% with 55% desorption within the first 8 BV. Concentration of NH_4-N in the first 8 BV was 460 mg/l which is a concentration factor of 14. During regeneration cycle 2, 68% of NH_4-N attached the zeolite surface was desorbed. During the 2nd cycle, regenerant NH_4-N in the first 8 BV was 870 mg/l; this is a concentration factor of 26. Regeneration with 8 BV is ideal as beyond this point excess solution is required to desorb a much smaller fraction of NH_4-N from the zeolite surface.

Regeneration eluate characteristics were evaluated such as pH and cation concentrations. The pH of the regeneration eluate will determine the need for pH adjustment prior to ammonia recovery. Metals contained in the regeneration eluate will impact the solids formed during struvite precipitation. Ion concentrations in the first 7 BV of regenerant can be found in Table A10. The first 7 BV of regeneration eluate had a pH of 8.7 and 7.7 in cycle 1 and 2, respectively. For vacuum ammonia distillation, the pH should be about 11 which mean that chemicals must be added to raise the pH. Future tests should be conducted with regeneration of zeolite at pH=12 to determine improvement in desorption and increase in regeneration eluate pH. Regenerant from the first 7 BV of cycle 1 and 2 contained 660 and 320 mg/l of K^+, respectively; these solutions also had 350 and 390 mg/l Ca^{2+}, respectively. Therefore, when utilizing this solution for struvite precipitation, there will be the potential to form calcium phosphates which inhibit struvite crystal growth; in addition, reducing Ca/Mg will increase P removal (Hwang and Choi, 1998; Wang *et al.*, 2005). Calcium solids formation could be prevented by operating struvite precipitation at pH less than 8.5 (Hao *et al.*, 2013).

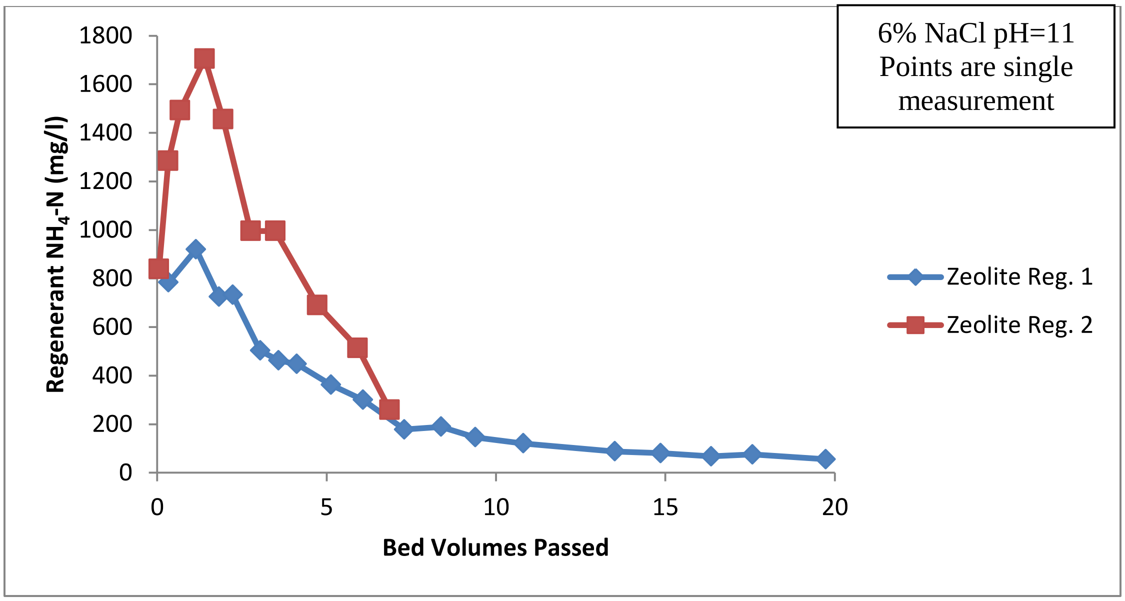


Figure 25: Zeolite regenerant NH_4-N concentration versus BV passed (cycle 1 and 2)

3.8 Struvite Precipitation

Potassium and N recovery through struvite precipitation is possible by combining the anion and cation regeneration streams. The resulting precipitate can be beneficially used as a fertilizer. Struvite and K-struvite precipitation studies using synthetic solutions were conducted in order to determine optimal pH for P removal. K-struvite could be formed using the same process if K recovery is desired. Precipitation of N-struvite is well defined in the literature; however, it was tested here for direct comparison to K-struvite. In K-struvite precipitation, the ratio of Mg:P:K was set to 1:1:1 and the initial solution was found to be within 2% of this target. Maximum P, Mg^{2+}, and K^{+} removal was at a pH of 12 as shown in Figure 26. Magnesium removal was 100% at pH=12 which means that it was the limiting ion in K-struvite precipitation. Based on a polynomial regression curve, the optimal pH for K-struvite precipitation was 11, which agrees with previous research (Xu *et al.*, 2011). The research conducted by Xu *et al*. (2011) also found that the Mg:K:P ratio should be 2:1:2 which explains the low P removal in the present study. K-struvite precipitation should be targeted if NH_4-N has been removed from the system. Therefore, the anion regenerant and liquid from vacuum ammonia distillation could be combined for K-struvite precipitation.

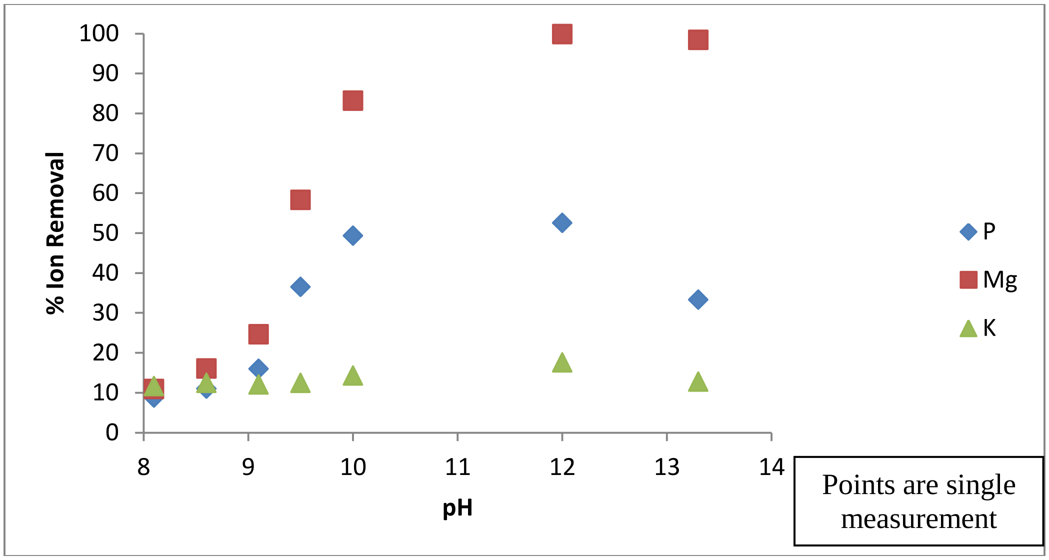


Figure 26: K-struvite precipitation vs pH using synthetic solution (Mg:P:N of 2:2:1)

During N-struvite precipitation, the ratio of Mg:P:N was 2:2:1. Removal of PO_4-P was greatest at pH=10 with about 97% removal as shown in Figure 27. Removal of PO_4-P was nearly 90% at pH 11 and 12, but then decreased significantly at pH=13. Magnesium appeared to be the limiting ion at pH>10 as 99% of magnesium was removed. Previous work has utilized Mg:P ratios of 1.3:1 or greater to achieve complete PO_4-P removal (Bhuiyan *et al.*, 2008). A wide range of pH have been reported for precipitation of struvite with 8.5-9 being optimal and greater than 90% removal possible at pH's as low as 7.3 (Wang *et al.*, 2005; Adnan *et al.*, 2003). N removal was only about 20% at pH's greater than 10. This is because as pH increases, precipitates other than struvite are formed in greater amounts (Hao *et al.*, 2013).

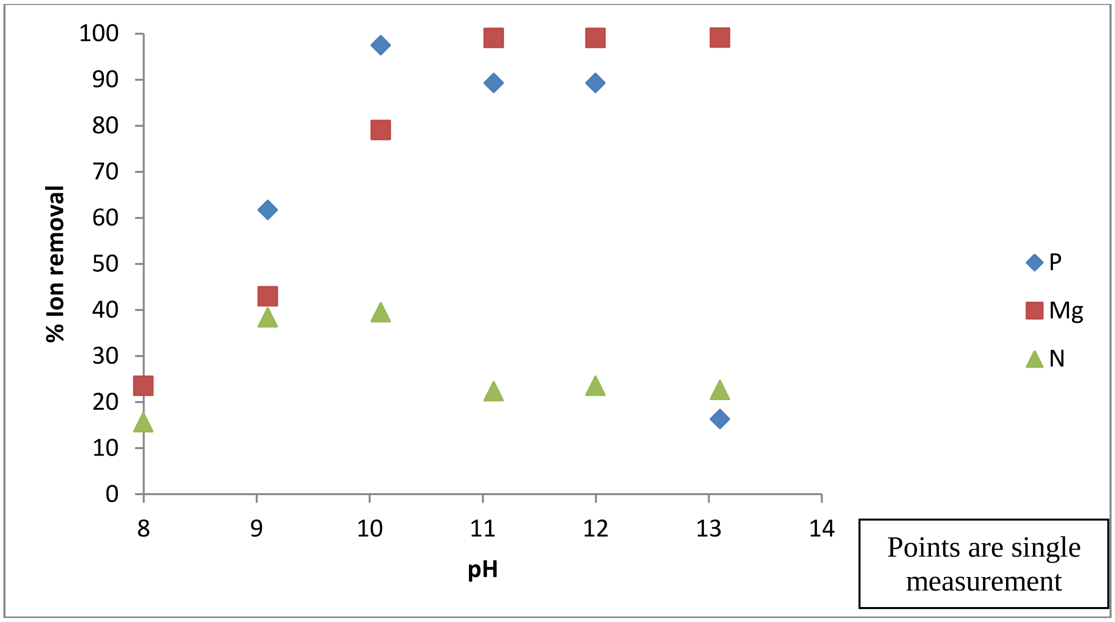


Figure 27: N-struvite precipitation vs pH using synthetic solutions

When operating struvite precipitation reactors, the reactor is typically seeded with struvite and can be operated based on the conditional solubility product (Britton *et al.*, 2005). Struvite conditional solubility product is calculated using Equation 5 which is described in Britton *et al.* (2005).

$$P_s = [Mg^{2+}]_e[NH_4^+ - N]_e[PO_4^{3-} - P]_e \qquad \text{Equation (5)}$$

Where,

P_s=Struvite conditional solubility product (mol^3/L^3)

$[Mg^{2+}]_e$=Equilibrium magnesium concentration (mol/L)

$[NH_4^+\text{-}N]_e$= Equilibrium NH_4-N concentration (mol/L)

$[PO_4^{-3}\text{-}P]_e$= Equilibrium PO_4-P concentration (mol/L)

The greater the conditional solubility product, the more struvite that potentially will be precipitated. This parameter is a function of pH. The $-\log_{10}(P_s)$ denoted as pP_s is graphed versus pH in Figure A4. The graph fits a second degree polynomial with an R^2 of 0.9223; line-of-best fit for this data is given in eqn. 4 and is similar to work done by Britton *et al.* (2005).

$$pP_s = -0.2351 * pH^2 + 5.4567 * pH - 22.59 \qquad \text{Equation (6)}$$

Where,

$pP_s=-\log_{10}(P_s)$

Conditional solubility product can be calculated using on-site using laboratory tests such as the batch testing conducted in this work. From eqn. 4, the optimal pH of the system based on given, Mg^{2+}, NH_4-N, and PO_4-P concentrations can be determined.

After precipitation of struvite from synthetic solutions, struvite was precipitated directly from zeolite regenerant, anion regenerant, and $MgCl_2$ solution. These batch tests will determine the amount of P that can be removed with a given Mg input as well as the impurities contained in the solids. Impurities can reduce the value of the recoverable. Solutions were added in a predetermined ratio to obtain an initial Mg:N:P ratio of 1:1:1. The pH in each precipitation reactor was adjusted to 10 after addition of all 3 solutions. Initial ion concentration and percent removal of each ion are listed in Table 11. Zeolite regenerant had large concentrations of NH_4^+, Mg^{2+}, Ca^{2+}, Na^+ and K^+ while the anion regenerants contained PO_4^{-3}, Al^{3+}, Fe^{2+}, and Cu^{2+}. All of these ions were of interest during precipitation reactions due to the potential of forming K-struvite and magnesium, calcium, sodium, aluminum, and iron phosphates in addition to the targeted solid, N-struvite. According to the data, 71% of P was recovered in the LayneRT™ precipitate. However, previous work has shown greater than 90% recovery (Sengupta and Pandit, 2011). This is likely due to limiting concentrations of Mg^{2+} for struvite precipitation as

96% of Mg^{2+} was removed. Magnesium limitation of struvite precipitation may also explain the low removal of NH_4^+. The solution started with Al^{3+} and Ca^{2+} concentration of 78 and 71 mg/l, respectively. Most Al^{3+} and Ca^{2+} were precipitated and therefore if aluminum and calcium phosphates are precipitating, the amount of struvite that forms will be limited. In the Dow-Cu regenerant precipitation reactions, less than 30% of P was removed. This may be caused by a limitation in reaction kinetics due to the low concentration of Mg^{2+} or other cations. Removal of Mg^{2+}, Ca^{2+}, and Fe^{2+} was still significant and may be in the hydroxide forms. Less than 15% of K^+ was removed in all systems, showing that K-struvite precipitation is not significant, but may be occurring. PO_4-P removal with Dow-FeCu regenerant struvite precipitation was 74%. Removal of N from Dow-FeCu + Zeolite regenerants was 21% which is lower than expected just as with the other precipitation tests.

Table 11: Removal % and initial ion concentration for anion + zeolite regenerant precipitation

Regeneration Eluate Source:	**LayneRT™**	**DOW-Cu 1**	**DOW-Cu 2**	**DOW-FeCu**
	% Removal	% Removal	% Removal	% Removal
PO_4-P	71	13	28	74
NH_4-N	19	10	16	21
Mg^{2+}	96	72	66	
Ca^{2+}	81	38	45	
Al^{3+}	92	39	58	
Fe^{2+}	76	80	79	
Cu^{2+}	59	13	9	
K^+	6	9	12	
PO_4-P	270	124	120	229
NH_4-N	121	54	53	103
Mg^{2+}	172	86	84	273
Ca^{2+}	71	32	31	65
Al^{3+}	78	0.2	0.3	0.1
Fe^{2+}	5.8	7.0	7.3	5.2
Cu^{2+}	0.28	6	21	12
K^+	132	59	58	54

Composition of solids from struvite precipitation of LayneRT™ and Dow-Cu 2 regenerant was analyzed by digesting the solids in nitric acid. Results are shown in Table 12 along with the composition of pure struvite for comparison. P content was similar to pure struvite for both regenerants; however, N content was only about 25% and 50% of pure struvite for LayneRT™ and Dow-Cu 2, respectively. Magnesium content was higher than pure struvite for LayneRT™ regenerant and Ca^{2+} and Al^{3+} were a significant portion of the solids. The magnesium to calcium ratio is about 2:1 in LayneRT™ precipitates. Calcium precipitation made up more than 25% of the solids content for Dow-Cu 2 and magnesium content was lower than pure struvite. Formation of calcium and aluminum phosphates reduces the amount of struvite precipitated and therefore explains the lower N removal with respect to P removal. From the data, it can be concluded that a significant portion of solids precipitated from LayneRT™ will contain Ca^{2+} and Al^{3+} thereby reducing the purity of the fertilizer and therefore the value. Calcium precipitation is even more significant in Dow-Cu 2 solids, which poses a concern for the value of the recoverable.

Table 12: Average solids composition for LayneRT™ and Dow-Cu 2 precipitation

	P	N	Mg	Ca	K	Fe	Al	Cu	Na
	%	%	%	%	%	%	%	%	%
LayneRT™	13.1	1.6	15.7	7	0.1	0.1	8.6	0.0	0.0
Dow-Cu 2	13.2	3.3	5.2	29	0.0	0.8	2.2	0.3	0.0
Pure Struvite	12.6	5.7	9.9	0	0	0	0	0	0

4 Conclusions

Conclusions from the batch and column IX testing as well as struvite precipitation are discussed below. The most significant findings from each testing method are listed in bullet points, with a detailed description of the conclusions following the bullet points.

4.1 Phosphate Ion Exchange Batch Testing Conclusions

- Batch testing greatest removal of P: Dow-Cu>Dow-FeCu> LayneRT™

During batch testing of anion media, it was determined that Dow-Cu, Dow-FeCu, LayneRT™, Dow-NAB-Cu, and Dow-HFO were the most effective with greater than 50% PO_4-P removal at an initial concentration of 100 mg/l PO_4-P. Dow-Cu out-performed all other resins with 76% removal of PO_4-P, the next closest being Dow-FeCu with 64% removal. Based upon previous column testing research, Dow-FeCu was expected to exchange the most PO_4-P; however, the lower removal may be due the acid/base pretreatment that removed iron particles from the resin or the kinetics of batch testing. For the Cu^{2+} loaded resins, eliminating the acid-base treatment step caused significant change in adsorptive capacity as Dow-NAB-Cu removed only 53% compared to the 76% of Dow-Cu; therefore, the extra chemicals required for preparation are likely worth the expense and time.

- Batch desorption of P (%): Dow-FeCu>Dow-Cu>LayneRT™
- Regeneration pH: Dow-FeCu (8), Dow-Cu (4.3), LayneRT™ (14)

Regeneration of the anion media following the 100 mg/l PO_4-P exchange cycle showed that greater than 49% of PO_4-P could be desorbed from Dow-Cu, Dow-FeCu, and LayneRT™. However, each of these resins requires a different regenerant solution.

LayneRT™ requires a high pH (14) solution for regeneration; batch testing with NaCl solution at pH=10, showed inadequate (<1%) PO_4^{-3} desorption during regeneration of LayneRT™. Previous work has shown that Dow-Cu and Dow-FeCu require a high salt concentration solution at pH=4.3. However, a neutral (pH=8) solution was used to regenerate Dow-FeCu in order to reduce acid requirements and meet the pH required for struvite precipitation. From the batch test results, the neutral pH was successful in regenerating Dow-FeCu. These conclusions raise a few questions such as: Is it possible to regenerate Dow-Cu at a neutral pH?; Is there more copper leaching with neutral pH regeneration?; What is the effect on subsequent IX capacity? A long-term batch or column study, greater than 15 cycles, would provide the answers to these questions.

4.2 Zeolite Ion Exchange Batch Testing Conclusions

- There is little difference in IX exchange capacity and NH_4-N desorption with 5%, 8%, and 10% NaCl regenerants.
- Regenerants with a pH>13 negatively impacted subsequent IX capacity of zeolite.
- Regenerants containing only $Ca(OH)_2$ or NaOH negatively impact subsequent IX capacity.
- Regenerants 8% NaCl (pH=8) and 7.5% NaCl (pH=12) provided statistically similar NH_4-N exchange and desorption.

NH_4-N exchange batch testing with zeolite showed that 5% NaCl concentration was a slightly less effective regenerant than 8% and 10% NaCl and that regenerant pH greater than 13 negatively affects subsequent IX capacity. NH_4-N removal after 3 IX cycles was 75%, 85%, and 83% for 5% NaCl, 8% NaCl, and 10% NaCl, respectively.

After 7 IX cycles, 7.5% NaCl + 0.5% NaOH was almost as effective as 8% NaCl solution. However, during intermediate cycles 7.5% NaCl + 0.5% NaOH was not nearly as effective. Calcium hydroxide was determined to be an ineffective regenerant as high concentrations resulted in calcium precipitates clogging the media and low concentrations were ineffective in regeneration. During mixed cation batch testing, exchange capacity of zeolite during all 7 cycles was similar for 8% NaCl and 7.5% NaCl (pH=12). A focus of future study may be to reduce the NaCl concentration from 7.5% while keeping the pH of 12 and determining if N exchange and desorption remain similar to the results of the present study.

4.3 Column Phosphate Ion Exchange Conclusions

- Exchange capacity of media: LayneRT™>Dow-FeCu>Dow-Cu
- Dow-HFO-Cu should be tested for comparison

All three anionic resins were able to sustain less than 0.075 mg/l effluent PO_4-P for more than 75 BV of influent wastewater containing approximately 4-6.5 mg/l PO_4-P. Prior to breakthrough (PO_4-P>0.075 mg/l), exchange capacity during column testing was 2000, 1490, and 455 mg P/L_{BV} for LayneRT™, Dow-FeCu, and Dow-Cu, respectively. LayneRT™ is purchased ready-to-use whereas the other resins must be prepared in the lab. However, LayneRT™ requires excessive amounts of NaOH to regenerate which may not be optimal for downstream processes and must be neutralized for disposal. Therefore, more chemical will be needed to neutralize the highly basic solution (pH>14). Leaching of metals is not significant with LayneRT™; however, Dow-Cu leaches copper up to 4 mg/l. Further testing should be conducted to determine the change in exchange capacity over numerous cycles. Also, Dow-HFO-Cu should be tested in column mode as it should have twice the capacity of LayneRT based on the literature.

- Desorption of P: LayneRT™ (89%), Dow-FeCu (91%), Dow-Cu (97%)
- Estimated (using regression curves) regeneration volume and PO_4-P concentration after 80% P desorption: LayneRT™ (3.5 BV, 550 mg/l P), Dow-FeCu (3BV, 650 mg/l P), Dow-Cu (1.1 BV, 400 mg/l P)
- Regeneration eluate pH: LayneRT™ (7 BV, pH=14), Dow-FeCu (4 BV, pH=9.6), Dow-Cu (4 BV, pH=9.9)
- The most significant leaching for each media was 155 mg/l Al^{3+} for LayneRT™, 7 mg/l Cu^{2+} for Dow-Cu, and 30 mg/l Cu^{2+} for Dow-FeCu.

Greater than 89% of PO_4-P exchanged was desorbed during regeneration of LayneRT™, Dow-Cu, and Dow-FeCu. In the first 7 BV, LayneRT regenerant PO_4-P concentration was 536 mg/l and the pH was 14. Therefore, IX with LayneRT™ concentrated PO_4-P by a factor of 130. Dow-Cu regenerant had a concentration of 150 mg/l PO_4-P in the first 4 BV; however, if only 1.5 BV of regenerant was used, the PO_4-P concentration would have been around 330 mg/l based on regression analysis. Dow-FeCu regenerant PO_4-P concentration was 559 mg/l after 4 BV; however, this concentration would be greater if less regenerant was utilized. With all resins there is a point of diminishing return. In other words, there is an optimal volume of regenerant at which enough PO_4-P has been desorbed to provide sufficient IX capacity for the next cycle and the PO_4-P concentration of the regenerant has not been diluted by passing excess regenerant through the column. Regeneration effluent pH in the first 4 BV was around 9.6-9.9 for both Dow-Cu and Dow-FeCu despite the difference in initial regenerant pH.

Aluminum leaching was 155 mg/l for LayneRT™ regenerant while copper leaching was 7 and 30 mg/l for Dow-Cu and Dow-Fe Cu, respectively. Leaching could cause decreased exchange capacity and impurities in struvite precipitates. According to the data, both Dow-FeCu and Dow-Cu provide regenerants near optimal pH for struvite precipitation, while LayneRT™ regenerant would require acid addition. Dow-FeCu requires the least pH adjustment chemicals; however, there is increased Cu leaching as compared to Dow-Cu.

4.4 Zeolite Ion Exchange Column Conclusions

- Zeolite NH_4-N exchange capacity: cycle 1 (4 g/L_{BV}), cycle 2 (6 g/L_{BV})
- Effluent NH_4-N was less than 0.2 mg/l during cycle 1 and >0.75 mg/l, but less than 1.5 mg/l during cycle 2.

Zeolite had an NH_4-N exchange capacity of 3.9 and 6.1 g/L_{BV} during IX cycle 1 and 2, respectively. In both cycles the influent NH_4-N concentration was about 32-34 mg/l and breakthrough occurred at 120 and 198 BV, respectively. Difference in IX capacity can mostly be attributed to the difference in influent cations; cycle 2 contained 36% less eq/l of K^+, Ca^{2+}, and Mg^{2+} combined. Exchange capacity difference may also be attributed to the difference in surface ions available for exchange. During IX cycle 1, there was a release of Na^+ and K^+ from the zeolite surface, whereas in cycle 2 only Na^+ was released from the surface. There was also a difference in effluent quality. During IX cycle 1 effluent NH_4-N was maintained well below 0.2 mg/l while IX cycle 2 was maintained above 0.75 mg/l, but below 1.5 mg/l. Column testing with more cycles may be necessary to provide additional data to determine if IX capacity change is from variation in ion concentration or regeneration characteristics.

- Desorption of NH_4-N: cycle 1 (74%), cycle 2 (68%)
- Regeneration eluate characteristics: cycle 1 (7 BV, NH_4-N=600 mg/l, pH=8.7), cycle 2 (7 BV, NH_4-N=740 mg/l, pH=7.7)

Greater than 74% NH_4-N desorption was found during regeneration cycle 1 and 2 using 6% NaCl (pH=11). The resulting brine solutions after 7 BV during cycle 1 and 2 contained 602 and 744 mg/l NH_4-N, respectively. Regenerant concentration likely increased due to increased NH_4-N exchange in IX cycle 2 and adsorbed NH_4-N remaining after regeneration cycle 1. Solution pH was 8.7 after cycle 1 and 7.7 after cycle 2. Therefore, pH adjustment may be necessary to meet struvite precipitation conditions and must be adjusted to about 11 for vacuum ammonia distillation. Future work should include multiple regeneration cycles to determine if effluent pH continues to be less than 9. Also, a column should be operated with regeneration at an increased pH, such as 12 or maybe 12.5, to determine the effect on regeneration effluent pH and subsequent IX capacity.

4.5 Struvite Precipitation Conclusions

- PO_4-P and NH_4-N removal (%) during batch struvite precipitation with zeolite regenerant, anion regenerant, and Mg^{2+} solution: LayneRT Regen. (P=74%, N=19%), Dow-FeCu Regen. (P=71%, N=21%), Dow-Cu Regen. 1 (P=13%, N=10%), Dow-Cu Regen. 2 (P=28%, N=16%)

- Solid precipitates P, N, Ca, Mg, Al, and Cu content (% m/m) for batch struvite precipitation with zeolite regenerant, anion regenerant, and Mg^{2+} solution: LayneRT Regen. (P=13%, N=2%, Mg=16%, Ca=7%, Al=9%), Dow-Cu Regen. 2 (P=13%, N=3%, Mg=5%, Ca=29%, Cu=0.3%)

Struvite precipitation in synthetic solutions was determined to be optimal at pH=10 and therefore anion and cation regenerants were mixed and adjusted to this pH for batch struvite precipitation. PO_4-P removal was 74%, 71%, 13%, and 28% for Dow-FeCu, LayneRT™, Dow-Cu 1, and Dow-Cu 2, respectively. Removal percentages may be limited by batch kinetics as the Dow-Cu precipitation flasks had initial PO_4-P concentration of about 120 mg/l, whereas the other two were greater than 200 mg/l. N removal was 19% and 21% for LayneRT™ and Dow-FeCu, respectively; however, for the two regenerants from Dow-Cu it was 10% and 16%. Based on the stoichiometrics, N removal should equal P removal if struvite was the precipitate. Therefore, other phosphate precipitates likely exist such as aluminum, calcium, and magnesium phosphates. Solids analysis revealed that the P content in LayneRT™ and Dow-Cu 2 precipitates were 13% which is similar to the 12.6% pure struvite contains; however, N content was only 3.3% and 1.6% in Dow-Cu 2 and LayneRT™ solids, respectively, whereas it should be 5.7%. Mg, Ca, and Al make up a large percentage of the LayneRT™ precipitates. The Al content is 9% which is likely much greater than desired for fertilizer use. Mg and Ca are the only other solids found in significant concentrations in Dow-Cu precipitate. More extensive precipitation studies are necessary to determine typical solids composition during precipitation reactions. This would include testing regenerants from many column cycles and testing regenerants at a range of pH’s.

4.6 Final Conclusions

In conclusion, IX with struvite precipitation is capable of removing P and N to meet low discharge limits while subsequently recovering P and N. However, the system must be improved from the current state of this research to be economical and applicable. Anion exchange media should be investigated further to determine the ability of DOW-HFO-Cu to remove P and be regenerated at a neutral pH. Long-term small-scale column studies should be conducted for comparison of IX capacity change in LayneRT™ and Dow-HFO-Cu. Regenerants should be similar to 2% NaCl + 2% NaOH, 6% NaCl (pH=8), and 6% NaCl (pH=12) for LayneRT™, Dow-FeCu, and zeolite, respectively. Operation of a zeolite column long term would determine change in IX capacity and regenerant characteristics in various cycles. Regenerant should be recycled in order to reduce chemical costs. Struvite precipitation should be improved to reduced impurities and improve P and N removal. Struvite precipitation of column regenerant should be conducted for many regenerant cycles and at a pH less than 9 using a seeded reactor. Solids content should be compared to desired fertilizer quality in various agricultural sectors. Lab-scale vacuum ammonia distillation tests should be conducted using sulfuric acid or water. The final pH and NH_4-N content should be determined during these studies. Ion exchange with recovery appears to be a technically feasible process; however, cost estimates for all processes will be necessary to determine the expense in comparison to conventional nutrient removal methods.

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Appendix A

Table A1: Nitrogen removal technology list

Nitrogen Removal Technology	Recoverables
Ammonia Distillation	Ammonium sulfate
Ammonia stripping	Ammonium sulfate
Vacuum membrane distillation	Ammonium sulfate
Algae	Biomass
Biological aerated filter	Biomass
Downflow-hanging sponge	Biomass
Fluidized bed bioreactor (FBBR)	Biomass
Moving bed biofilm reactor (MBBR)	Biomass
Rotating biological contactor	Biomass
Sequencing batch reactor	Biomass
SHARON-Anammox	Biomass
Trickling filter	Biomass
Upflow submerged	Biomass
Electrodialysis	Concentrated solution
Ion Exchange	Concentrated solution
Breakpoint chlorination	None
Electrochemical Oxidation	None
Duckweed	Plant biomass
Struvite	Struvite

Table A2: Phosphorus removal technology list

Phosphorus Removal Technology	Recoverables
Algae	Biomass
Enhanced biological phosphorus removal	Biomass
Adsorption	Concentrated solution
Electrodialysis	Concentrated solution
Ion exchange	Concentrated solution
Iron-Oxide Coated Filtration	Ferric phosphate sludge
Precipitation w/ alum, ferric, lime, PACl	Metal phosphate sludge
Ballasted Flocculation	Phosphate sludge
Thermal-metallurgical	Phosphorus ash
Wet chemical	Phosphorus ash
Duckweed	Plant biomass
Struvite	Struvite

Table A3: Student t-test results for zeolite IX in mixed cation solution (IX cycle 5)

P-values	**0.1% NaOH**	**8% NaCl**	**7.5% NaCl pH=12**
8% NaCl	0.026		
7.5% NaCl pH=12	0.014	0.735	
0.1% $Ca(OH)_2$	0.002	0.0008	0.0004

Table A4: P-values for F-test of zeolite IX in mixed cation solution (IX cycle 5)

P-values	**0.1% NaOH**	**8% NaCl**	**7.5% NaCl pH=12**
8% NaCl	0.0065		
7.5% NaCl pH=12	0.812	0.0044	
0.1% $Ca(OH)_2$	0.299	0.036	0.215

Table A5: P-values for F-test of spiked phosphate IX

	DOW-Acid/Base-Cu	DOW-FeCu	LayneRT	DOW-Cu	DOW-HFO	AA neutral	AA basic
DOW-FeCu	0.15						
LayneRT	0.13	0.86					
DOW-Cu	0.21	0.70	0.58				
DOW-HFO	0.41	0.45	0.39	0.60			
AA neutral	0.15	1.00	0.87	0.70	0.45		
AA basic	0.20	0.75	0.63	0.94	0.57	0.75	
DOW-Mn-Alum	0.28	0.45	0.36	0.70	0.79	0.45	0.65

Table A6: Student t-test p-values for spiked phosphate regeneration

	DOW -Cu	DOW-FeCu	LayneRT™	DOW-NAB-Cu	DOW-HFO	AA neutral
DOW-FeCu	0.30					
LayneRT™	0.080	0.0063				
DOW-Cu	0.0089	0.0005	0.015			
DOW-HFO	0.0061	0.0002	0.0009	0.0011		
AA neutral	0.0061	0.0004	0.0048	0.076	0.0053	
AA basic	0.55	0.22	0.72	0.16	0.047	0.075

Table A7: P-values for F-test of spiked phosphate regeneration

	DOW-Acid/Base-Cu	DOW-FeCu	LayneRT	DOW-Cu	DOW-HFO	AA neutral
DOW-FeCu	0.42					
LayneRT	0.40	0.96				
DOW-Cu	0.25	0.69	0.72			
DOW-HFO	0.30	0.58	0.60	0.78		
AA neutral	0.12	0.36	0.38	0.59	0.91	
AA basic	0.96	0.45	0.43	0.28	0.31	0.13

Table A8: SSWRF Secondary Effluent Characteristics

NH_4-N	mg/l	1.5	Be	µg/l	ND[2]
TP	mg/l	0.4	Cr	µg/l	ND
PO_4-P	mg/l	0.2	Mn	µg/l	ND
orgP	mg/l	0.2	Fe	mg/l	ND
Alkalinity	mg/l as $CaCO_3$	267	Co	µg/l	ND
BOD_5	mg/l	12	Ni	µg/l	ND
BOD_L	mg/l	18	Cu	µg/l	18
Cl^-	mg/l	90	Zn	µg/l	ND
SO_4-S	mg/l	26	As	µg/l	ND
S^{2-}	mg/l	7	Se	µg/l	ND
NO_3-N	mg/l	3.9	Mo	µg/l	ND
K^+	mg/l	79	Ag	µg/l	ND
Ca^{2+}	mg/l	9	Cd	µg/l	ND
Mg^{2+}	mg/l	36	Hg	µg/l	ND
Na^+	mg/l	158	Pb	µg/l	ND
Al	µg/l	124			

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[2] ND-Non detect or below detection limit

Table A9: Anion IX effluent metals

LayneRT™	Na	Mg	Al	K	Ca	Mn	Cu
BV	mg/l	mg/l	µg/l	mg/l	mg/l	µg/l	µg/l
0	123.5	26.2	44.9	7.7	68.0	9.0	36.0
238	117.6	27.2	35.8	7.1	60.2	4.6	35.6
475	122.6	28.3	22.7	7.5	66.9	4.2	39.5
DOW-Cu 1	130.1	29.7	49.1	9.8	67.1	105.1	2949.3
	127.9	29.4	26.7	9.6	65.8	103.3	1238.0
	127.6	29.3	70.3	9.5	65.7	84.2	1340.9
	127.1	29.1	47.1	9.5	65.5	72.0	919.8
Dow-Cu 2	127.4	29.4	116.4	9.5	66.5	89.9	3603.0
	128.4	29.3	54.5	9.5	65.3	84.4	1092.1
	128.7	29.5	37.3	9.6	65.9	80.8	1274.4
	130.3	29.9	489.4	9.8	65.9	72.5	1036.0

Table A10: Ion concentrations in anion and zeolite regenerants

	Volume	**PO_4-P**	**Al**	**Cu**	**Fe**	**Na**	**Ca**
	mL	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
LayneRT™	250	536	155	0.49	8.0	12873	0.1
DOW-Cu 1	140	151	0.23	6.7	7.6	17155	0.1
DOW-Cu 2	140	150	0.33	26	8.2	16707	0.1
DOW-FeCu	140	559	0.25	30	9.1	17130	11
Zeolite 1	250		0.22	0.15	8.6	13323	353
Zeolite 2	250		0.23	0.16	11	16239	392
	Volume	**NH_4-N**	**Mg**	**K**	**Mn**	**Ni**	**Mo**
	mL	mg/l	mg/l	mg/l	µg/l	µg/l	µg/l
LayneRT™	250		0.40	0	51	482	417
DOW-Cu 1	140		1.5	0	78	255	223
DOW-Cu 2	140		1.8	0	46	125	164
DOW-FeCu	140		2.5	0	x	107	x
Zeolite 1	250	602	23	655	80	121	0
Zeolite 2	250	744	24	318	74	155	x

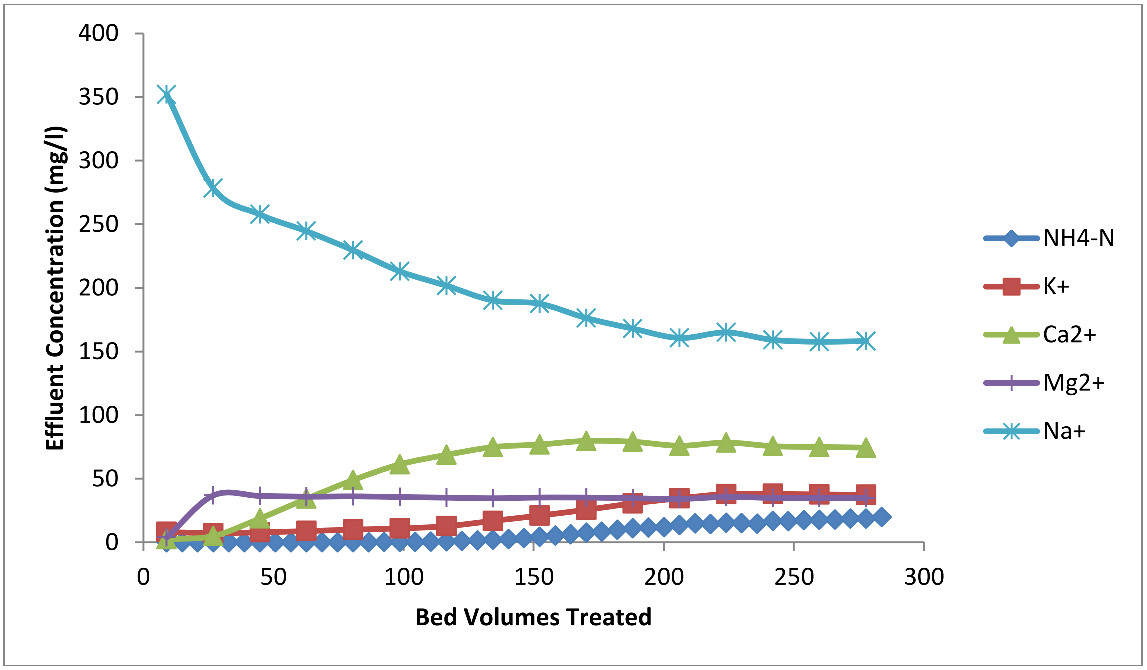

Figure A1: Zeolite IX cycle 1 effluent cations vs BV treated.

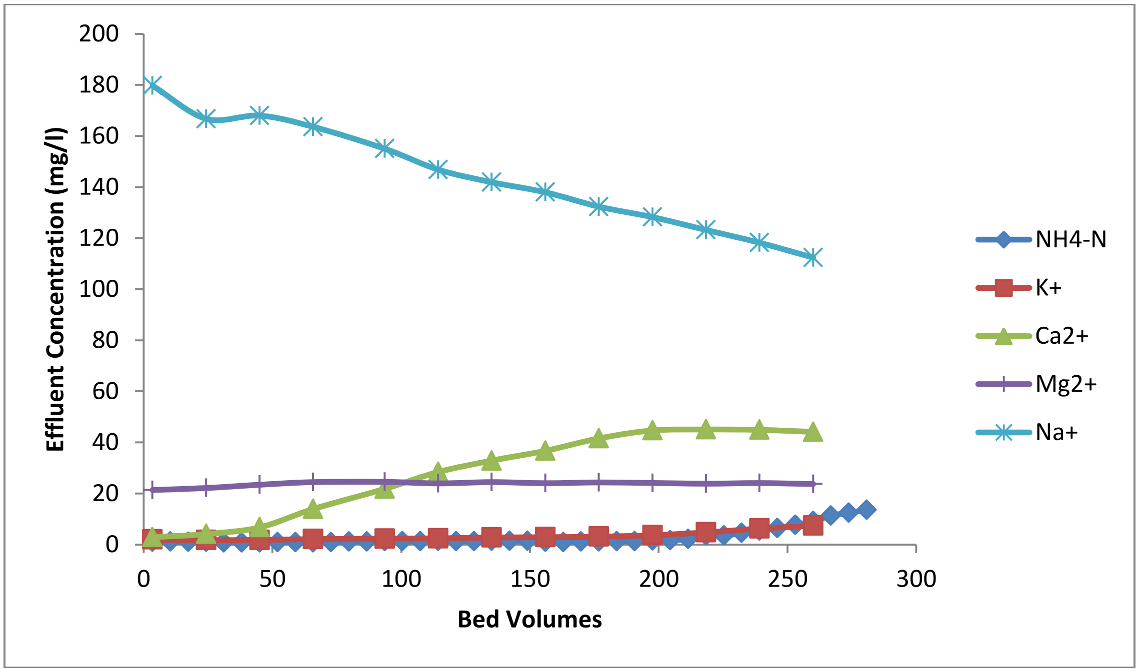

Figure A2: Zeolite IX cycle 2 effluent cations vs BV treated

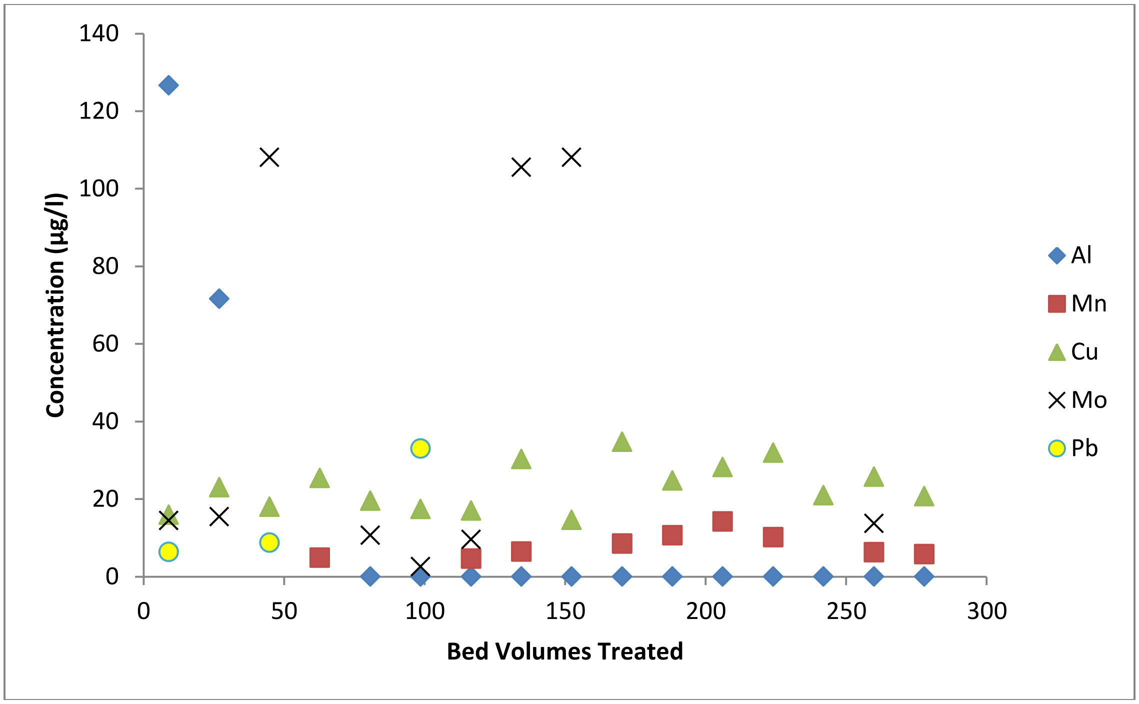

Figure A3: Zeolite IX cycle 1 effluent metals vs BV treated

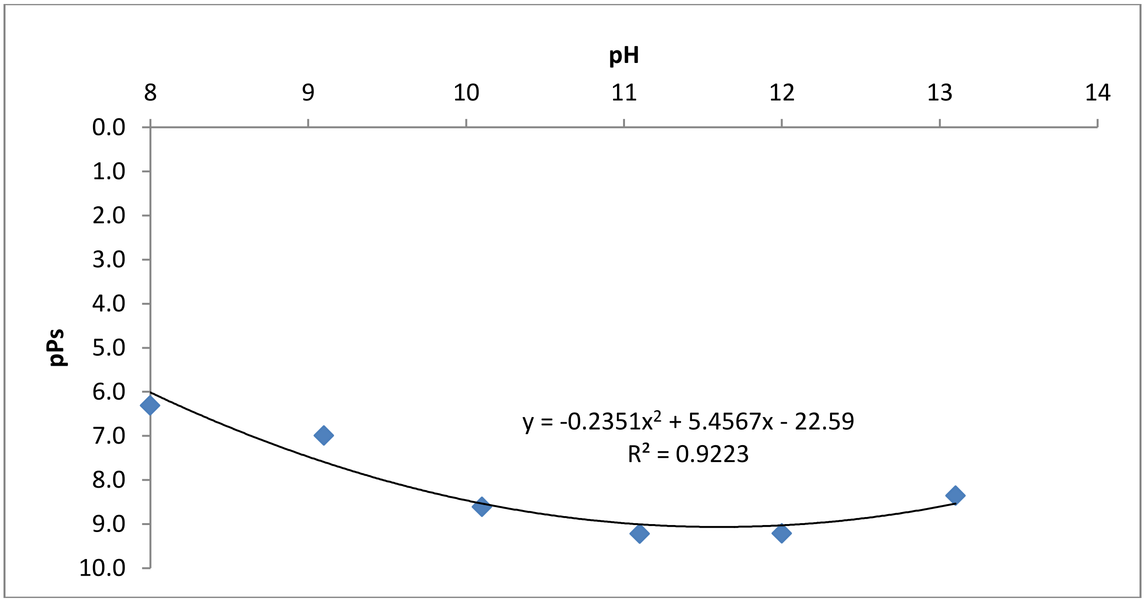

Figure A4: Conditional struvite solubility product vs pH for synthetic solution N-struvite precipitation